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XIV.—ON SOME REDUCTIONS WITH ZINC AND AMMONIA.

BY W. G. MIXTER.

Zinc and a solution of an ammonium salt, the nitrate excepted, and zinc with iron or platinum and ammonia water, evolve hydrogen. The reaction has been long known, but has been little used for reducing nitro bodies or for adding hydrogen. If finely divided zinc be placed in aqueous or alcoholic ammonia, and a little platinum chloride solution be added, hydrogen will come off slowly for a long time. The platinum precipitates on the zinc and the two metals form a galvanic couple. The small amount of ammonium chloride present doubtless hastens the action. If an alcoholic solution of a halogen or nitro organic compound be added the action increases, and the mixture often becomes warm. Metnitraniline, dinitrobenzene, dinitrotoluene and nitrotoluidine were each dissolved in alcohol, and some strong ammonia, a liberal quantity of pulverized zinc[1] and a little platinum solution were added. The result of each experiment was a substance which blackened on exposure to the air. Nitrobenzene in an alcoholic

[1] The zinc was pulverized by pouring the molten metal into a mortar and pounding as soon as it had solidified.

solution was subjected to the action of platinized zinc and ammonia for several days. After a time red crystals of azobenzene appeared. To the clear solution sulphuric acid was added, and from the precipitate benzidine was separated by means of ammonia.

Paraazoxyacetanilide.

Paranitracetanilide[1] was dissolved in a flask in about twenty parts of alcohol; from four to ten parts of concentrated ammonia water and from four to ten parts of pulverized zinc were added, and then a few cubic centimetres of platinum chloride solution were poured in. The mixture became warm in a few minutes, and in course of half an hour the azoxyacetanilide appeared as a yellow fibrous mass. After a couple of hours the evolution of gas was less rapid, and the liquid became cold. The flask was shaken occasionally to prevent the zinc from caking together, and was warmed a few times to hasten the action. After not less than three days, the azoxyacetanilide was filtered off, washed with alcohol, and then shaken up with very dilute hydrochloric acid to remove any zinc compounds which may have been present. After filtering again, and thoroughly washing with water, the substance was dissolved in boiling alcohol and filtered hot. The azoxyacetanilide separates as the solution cools in minute hair-like particles, which are thoroughly washed with alcohol. The yield was about one-half the weight of the nitranilide used. The duplicate analyses are of two different preparations of substance, dried first at common temperatures, and lastly at 100° C.

I. 0.4266 gram gave 0.9638 gram of CO_2 and 0.2028 gram of H_2O.

II. 0.3876 gram gave 59.3 cc. of N at 16° C. and 760 mm. pressure.

III. 0.5365 gram gave 1.2077 gram of CO_2 and 0.2570 gram of H_2O.

IV. 0.3722 gram gave 59.8 cc. of N at 25° C. and 758 mm. pressure.

[1] The crude nitranilide, obtained by dissolving acetanilide in well cooled fuming nitric acid, was washed with water, and finally with dilute ammonia to remove any phenole bodies. It was then boiled with repeated portions of water, filtered, and the products from cooling the different solutions kept separate. The crystals obtained from the last two or three boilings were paranitracetanilide, which melted at 207° C. and which gave on boiling with potash no orthonitraniline, but paranitraniline. The crude nitranilide yielded by this treatment a small portion of orthonitraniline.

	Calculated for $C_{16}H_{16}N_4O_2$.	I.	II.	III.	IV.
C	61.54	61.61	...	61.39	...
H	5.13	5.28	...	5.32	...
N	17.95	...	18.15	...	18.40

The substance is formed by the removal of three atoms of oxygen from two molecules of nitracetanilide. From the apparent analogy of its formation to that of azoxybenzene from nitrobenzene the compound is paraazoxyacetanilide, having the formula $C_6H_4NHC_2H_3ON$ / $C_6H_4NHC_2H_3ON$ >O. This view is also supported by the facts that the acetyl groups can be replaced by hydrogen and then the N_2O converted into amido groups with the formation of paraphenylenediamine. The paraazoxyacetanilide melts at 275–278° C., has a light golden yellow color, and is sparingly soluble in boiling and very slightly soluble in cold alcohol.

The alcoholic ammonia filtrate from the azoxyacetanilide was poured back into the zinc, and after several days the solution was evaporated. A black residue remained and nothing definite was obtained.[1]

Metanitracetanilide, from metanitraniline and acetyl chloride, yielded on reducing with zinc and ammonia in one experiment a substance which gave analytical results that corresponded closely with the composition of equal molecules of azoxyacetanilide, $C_{16}H_{16}N_4O_3$, and azoacetanilide, $C_{16}H_{16}N_4O_2$. Further investigation may lead to satisfactory results.

Paraazoxyaniline.

Paraazoxyacetanilide dissolves readily in a hot concentrated solution of potash in alcohol, and when part of the alcohol has been boiled off small red crystals separate. After most of the alcohol has been expelled the potash may be washed out with cold water, and the substance after drying at 100° C. is quite pure.

I. 0.5074 gram gave 1.1761 gram of CO_2 and 0.2431 gram of water.

II. 0.2880 gram gave 59.5 cc. of N at 17° C. and 771 mm. pressure.

III. 0.3181 gram gave 66.83 cc. of N at 17° C. and 766 mm. pressure.

[1] Since this paper went to press the preparation of azoxyacetanilide has been repeated, and from the alcoholic ammonia filtrate azoacetanilide, $C_{16}H_{16}N_4O_2$, has been separated. It will be described in a future article.

	Calculated for $C_{12}H_{12}N_4O$.	I.	II.	III.
C	63.16	63.21	...	...
H	5.27	5.23	...	...
N	24.56	...	24.78	25.04

The potash effects the replacement of the acetyl group by hydrogen, and assuming that the formula given to the azoxyacetanilide represents its constitution the new body is $\begin{matrix} C_6H_4NH_2N \\ | \\ C_6H_4NH_2N \end{matrix}\!>\!O$, para-azoxyaniline, a diamido azoxybenzene. It is an analogue of Buckney's azoxytoluidine.[1] Paraazoxyaniline melts at 182–184° C., dissolves rapidly in alcohol, giving a red solution, is sparingly soluble in boiling water, and separates on cooling as a fibrous yellow mass. The hydrochloride crystallizes well from aqueous solution and is sparingly soluble in alcohol. The sulphate separates on adding sulphuric acid to a dilute solution of the azoxyaniline. These two salts are nearly white, tinged with red. The platinum salt was made by adding platinum chloride to a hot alcoholic solution of the hydrochloride. Long brownish red needles separated immediately, which were filtered after cooling and washed with alcohol and dried at 100° C. 0.1712 gram of the salt left after ignition 0.0528 gram of platinum, 30.85 per cent.; theory requires for $C_{12}H_{12}N_4O$, H_2PtCl_6 30.82 per cent. of platinum. The azoxyaniline is reduced to paraphenylenediamine when heated for several hours to 100° C. with alcoholic ammonium sulphide in a sealed tube. Tin and hydrochloric acid effect the same reduction rapidly. In one experiment the tin was separated as sulphide and the solution was evaporated, and the chlorine in the salt obtained was found to be 39.06 per cent.; theory requires 39.19 per cent. of chlorine in $C_6H_4(NH_2)_2H_2Cl_2$. The phenylenediamine separated from the hydrochloride by distillation with sodium carbonate, Biedermann and Ledoux's method; melted at 140° C.

As azoxybenzene yields azobenzene and hydrazobenzene, we may expect azoxyaniline, which is diamidoazoxybenzene, to be changed by reducing agents to the known substances, diamidoazobenzene and diamidohydrazobenzene. These bodies have, however, not been obtained from the azoxyaniline. In one experiment red azoxyaniline was dissolved in alcoholic ammonia and the solution was then saturated with hydrogen sulphide. After a day the

[1] Ber. d. deutsch. chem. Gesell. **11**, 1452.

alcohol was boiled off and the dry residue was treated with hot dilute hydrochloric acid, and the solution was filtered from the small quantity of sulphur which remained. The base was precipitated by ammonia, and was dark green. It was dried at 100° C. The analysis shows no change in the composition of the azoxyaniline treated, as described, with ammonium sulphide.

I. 0.4298 gram gave 0.9913 gram of CO_2 and 0.2062 gram of H_2O.

II. 0.3172 gram gave 65 cc. of N at 14° C. and 770 mm. pressure.

	Calculated for $C_{13}H_{12}N_4O$.	I.	II.
C	63.16	62.90	...
H	5.27	5.33	...
N	24.56	...	24.80

This green substance, after recrystallization from boiling water, melted at about 191° C. The hydrochloride and sulphate are green. Its platinum salt, prepared as before described, separated as rather a slimy mass, and after drying had a light grayish tint. It yielded 30.61 per cent. of platinum. Tin and hydrochloric acid reduced the green substance analyzed to paraphenylenediamine. While the color, melting point and the character of its platinum salt indicate that this green substance is a different modification from the azoxyaniline first described, it is probably the same compound colored green by some body formed by the action of the ammonium sulphide. The red azoxyaniline gave on boiling both its aqueous and alcoholic solutions through which a current of sulphur dioxide was passing, green solutions, which did not react for sulphuric acid, an indication that there had been no reduction. The residues left after evaporation were green.

Metaazoxybenzanilide.

20 grams of metanitrabenzanilide, from metanitraniline and benzoyl chloride, were dissolved in 300 cc. of boiling alcohol, and then 200 cc. of alcohol saturated with ammonia; 300 grams of pulverized zinc and 1 gram of platinum in solution were added. Gas was freely evolved, and in half an hour the precipitate was quite thick. After standing twenty-four hours the mixture was heated to boiling, filtered hot, and the substance was digested with a fresh portion of boiling alcohol and washed with alcohol. It was then shaken up with water to remove the zinc particles as much as pos-

sible, and next treated with dilute hydrochloric acid. It was finally washed with water and dried at 100° C. The product was an exceedingly light powder of a pale yellow color.

I. 0.4671 gram gave 1.233 gram of CO_2 and 0.2075 gram of H_2O.

II. 0.4168 gram gave 1.1045 gram of CO_2 and 0.1851 gram of H_2O.

III. 0.366 gram gave 39.9 cc. of N at 15° C. and 762 mm. pressure.

	Calculated for $C_{26}H_{20}N_4O_3$.	I.	II.	III.
C	71.56	71.99	72.27	...
H	4.58	4.93	4.93	...
N	12.85	...	...	12.98

The formula $\begin{matrix} C_6H_4NHC_7H_5ON \\ | \\ C_6H_4NHC_7H_5ON \end{matrix}\!\!>\!O$ represents the constitution of the substance as analogous to that of azoxyacetanilide. The azoxybenzanilide melts at about 272° C. It is insoluble or nearly insoluble in alcohol, ether and benzene. It was treated with a boiling solution of potash in alcohol, and a substance soluble in alcohol was the result; and from the nitrogen found in this substance it appeared that only one benzoyl group had been separated. Warm oil of vitriol dissolves the azoxybenzanilide and sets free benzoic acid, but the product of the reaction was too small for satisfactory investigation.

It may be stated that in the first attempt to prepare the meta-azoxybenzanilide the mixture was exposed to the zinc for several days, and the substance which separated from the solution was treated as already described. Duplicate analyses showed that the reduction had gone further than required for the formation of an azoxy-compound, and indicated a mixture of equal molecules of azoxybenzanilide and azobenzanilide, a result analogous to that obtained in the reduction of the metanitracetanilide. The alcoholic filtrate from the azoxybenzanilide was poured back on to the zinc and left for two or three weeks. No further precipitation took place, and the solution on evaporation left a tarry mass which dissolved readily in boiling water. The crystals which separated on cooling are Bell's compound $C_6H_4NH_2NHC_7H_5O$,[1] as the following results show:

[1] Ber. d. deutsch. chem. Gesell. **7**, 497.

	Theory.	Found.
C	73·58	73·37
H	5.66	5.56
N	13.30	13.11

The platinum salt yielded 23.03 per cent. of platinum. Bell's salt requires 23.77 per cent. Bell gives the melting point at 125° C. and the writer's preparations melted at 124° C.

The following formulae show the analogy between the derivatives of nitrobenzene and those obtained from the nitranilides.

Nitrobenzene $C_6H_5NO_2$ Nitracetanilide $C_6H_4NHC_2H_3ONO_2$

Azoxybenzene $\begin{matrix} C_6H_5N \\ | \\ C_6H_5N \end{matrix}\!>\!O$ Azoxyacetanilide $\begin{matrix} C_6H_4NHC_2H_3ON \\ | \\ C_6H_4NHC_2H_3ON \end{matrix}\!>\!O$

Azoxyaniline $\begin{matrix} C_6H_4NH_2N \\ | \\ C_6H_4NH_2N \end{matrix}\!>\!O$

Azobenzene $\begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix}$

Hydrazobenzene $\begin{matrix} C_6H_5NH \\ | \\ C_6H_5NH \end{matrix}$

Aniline $C_6H_5NH_2$ Phenylenediamine $C_6H_4NH_2NH_2$

Nitrobenzanilide $C_6H_4NHC_7H_5ONO_2$

Azoxybenzanilide $\begin{matrix} C_6H_4NHC_7H_5ON \\ | \\ C_6H_4NHC_7H_5ON \end{matrix}\!>\!O$

Amidobenzanilide $C_6H_4NHC_7H_5ONH_2$

The combustions for the carbon and hydrogen estimations were made with copper oxide and completed with oxygen gas; the nitrogen was determined by Dumas' method with the aid of a Sprengel pump and a Schiff azotometer.

XV.—ON THE DISTRIBUTION OF ARSENIC IN A HUMAN BODY.

By R. H. Chittenden.

A recent judicial investigation into the cause of death in a certain case[1] (J. C.) resulted in the finding of sufficient arsenic in the internal organs to warrant the belief that the entire body contained what would ordinarily constitute a fatal dose of this poison. Nearly six months after burial the body was disinterred, weighed, and nearly one-half of the entire muscle and bony tissue removed for further examination: the object being to ascertain the actual amount of arsenic in the whole body, and at the same time to glean all possible facts relative to the distribution of the poison.

It rarely happens that such a complete and exhaustive chemical analysis is called for in judicial investigations, and thus we find on record but few instances where a poison is sought for quantitatively through the entire body; and yet the results of such a search, in the writer's opinion, may be of primary importance in answering some of the questions which the finding of poison in a human body naturally suggests: In what form was the poison taken? How long had it been in the body before death? Was the person habituated to the use of the poison? etc. These are a few of the questions which, in the case of arsenic at least, call for a decisive answer. Improved chemical methods which give us the means of accurately determining even minute quantities of arsenic, and our knowledge of the absorption and elimination of this poison as gleaned by physiological experiments on animals, give us data which ought to enable us in many cases to draw accurate and concise conclusions.

The results obtained in this investigation have therefore seemed of sufficient scientific importance to merit a somewhat detailed description; for however important physiological experiments on animals may be, and however trustworthy the results obtained are to the scientific man, still from a judicial point of view data regarding the relative absorption of poisons, etc., in the human body are of even greater weight and value.

[1] The body was found floating in the shallow water on a sandy beach. The body bore no evidences of having been long in the water, and a careful autopsy made by Dr. T. M. Prudden failed to reveal the cause of death. Portions of the various internal organs removed at this time were placed in alcohol and preserved separately for chemical analysis.

The method of analysis consisted in oxidizing a weighed amount of the sampled organic matter with nitric and sulphuric acids at elevated temperatures, the arsenic being ultimately obtained and weighed in the metallic state.[1] From the amount of arsenic found in the portion examined, the content of the entire organ or portion of tissue was calculated. The result, when possible, was verified by a duplicate analysis, while in several instances the content of the entire tissue was calculated from the average of two or more determinations. Such of the internal organs as had been placed in alcohol were sampled for analysis by being cut into fine pieces and then ground to a thick paste with the alcohol[2] in a mortar. The sampling of the muscle and bony tissue was effected by the use of pure nitric acid, with the aid of a gentle heat, by means of which the muscle and bones were entirely dissolved. The method of sampling tissue or large organs in this manner, in toxical investigations, particularly for arsenic, has yielded the writer excellent results, since the confirmation of duplicated analyses so obtainable greatly diminishes the possibility of error, and thus adds greater weight to the chemical testimony.

Following are the quantitative results obtained:[3]

Entire stomach[4] *with contents and esophagus.* Weight, 603 grams. (1) 100 grams sampled substance gave .0013 gram metallic arsenic. (2) 106 grams sampled substance gave .00135 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .158 grain.

Entire large and small intestines with contents and alcohol.— Weight, 1471 grams. (1) 200 grams sampled substance gave .0021 gram metallic arsenic. (2) 671 grams sampled substance gave .0122 gram arsenious sulphide. Calculated from No. 1, total arsenious oxide = .314 grain.

Both kidneys. Weight when dried, 83 grams. Entire substance gave .0015 gram metallic arsenic = .029 grain arsenious oxide.

Liver (one-half). Weight with alcohol, 1482 grams.[5] 110 grams sampled substance gave .0004 gram metallic arsenic, total arsenious oxide = .109 grain.

[1] For full description of process, see this Journal, **2**, 235.

[2] An examination being also made for alkaloid poisons.

[3] It is hardly necessary to state that the arsenic was subjected to all the known tests to prove its identity. Likewise the metallic arsenic weighed was in many cases converted into other known forms and again weighed.

[4] The mucous membrane of the stomach was entirely free from any signs of inflammation.

[5] Weight of liver free from alcohol, 707 grams.

Brain (one-third). Weight with alcohol, 336 grams. (1) 200 grams sampled substance gave .0007 gram metallic arsenic. (2) 136 grams sampled substance gave .0005 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .0255 grain.

Lungs and spleen[1] (two-thirds). Weight moist tissue, 331 grams. (1) 100 grams sampled substance gave .0017 gram metallic arsenic. (2) 131 grams sampled substance gave .0022 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .1146 grain.

Heart (one-fourth). Weight with alcohol,[2] 411 grams. Entire substance gave .0014 gram metallic arsenic = .028 grain arsenious oxide.

Trachea, larynx and tongue. Weight dried tissue, 175 grams. Entire substance gave .004 gram metallic arsenic = .081 grain arsenious oxide.

Diaphragm. Weight dried tissue, 155 grams. Entire substance gave .0005 gram metallic arsenic = .01 grain arsenious oxide.

Total quantity of arsenious oxide found in internal organs:

Stomach and esophagus	.158 grain.
Liver (one-half)	.109 "
Intestines	.314 "
Kidneys	.029 "
Heart (one-fourth)	.028 "
Lungs and spleen (two-thirds)	.1146 "
Brain (one-third)	.0255 "
Trachea, larynx and tongue	.081 "
Diaphragm	.010 "
	.8691 "

The remaining portions of liver, heart, brain, lungs and spleen, not preserved for analysis, would give by calculation the following quantities of arsenic, assuming that the poison was evenly distributed through these various organs:

One-half of the liver	.109	× 1 =	.109 grain.
Three-fourths of the heart	.028	× 3 =	.084 "
Two-thirds of the brain	.025	× 2 =	.050 "
One-third of lungs and spleen	.1146	÷ 2 =	.0573 "
			.3003 grain.
Arsenious oxide actually found			.8691 "

Total arsenious oxide in internal organs is therefore 1.1694 grain.

[1] Portions of lungs, heart and spleen were preserved in one jar. The heart with all of the alcohol was examined in one portion, the lungs and spleen in another.

[2] Weight of heart freed from alcohol, 33 grams.

Left arm. Total weight, 1230 grams. (1) 100 grams sampled tissue gave .0004 gram metallic arsenic. (2) 100 grams sampled tissue gave .00035 gram metallic arsenic. (3) 300 grams sampled tissue gave .0011 gram metallic arsenic. Calculated from the average of Nos. 1 and 2, total arsenious oxide = .094 grain.

Right leg (except thigh bone). Total weight, 4650 grams. (1) 100 grams sampled tissue gave .00012 gram metallic arsenic. (2) 100 grams sampled tissue gave .00012 gram metallic arsenic. (3) 400 grams sampled tissue gave .0005 gram metallic arsenic. Calculated from No. 3, total arsenious oxide = .118 grain.

Thigh bone of right leg. Weight of cleaned bone, 216 grams. Entire substance failed to give any arsenic.

Transverse section of body at pelvis, including pelvic bones.— Total weight, 4060 grams. (1) 100 grams sampled tissue gave .0002 gram metallic arsenic. (2) 100 grams sampled tissue gave .00025 gram metallic arsenic. Calculated from the average of these two determinations, total arsenious oxide = .186 grain.

Muscle from breast, right side. Total weight, 510 grams. (1) 200 grams sampled tissue gave .0019 gram metallic arsenic. (2) 310 grams sampled tissue gave .00255 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .098 grain.

Muscle from back, left side. Total weight, 620 grams. (1) 200 grams sampled tissue gave .00565 gram metallic arsenic. (2) 200 grams sampled tissue gave .00565 gram metallic arsenic. (3) 200 grams sampled tissue gave .0056 gram metallic arsenic. Calculated from No. 1, total arsenious oxide = .356 grain.

Summary of the Examination of Muscle and Bony Tissue.

	Total weight.	Total As_2O_3.
Left arm	2 lbs. 11½ oz.	.094 grain.
Right leg, except thigh bone	10 4	.118
Thigh bone	7½	...
Transverse section . . .	8 15½	.186
Muscle from breast . . .	1 2½	.098
Muscle from back . . .	1 6	.356
	22 lbs. 46½ oz.	.852 grain.
	24 14½ = 398.5 oz.	

The entire body, aside from the internal organs, weighed at the time of disinterment 57 pounds = 912 oz. Thus the proportion,

$$398.5 : 912 :: .852 : x = 1.9498 \text{ grains } As_2O_3$$

must give the total amount of arsenious oxide contained in the entire muscle and bony tissue, provided the portions analyzed represent average samples. Naturally care must be taken to avoid an undue proportion of muscle, since this is invariably richer in arsenic than the bones. In the present instance the only question would be in regard to the bones of the trunk and skull, since one of each pair of limbs was analyzed. The transverse section, however, with the heavy pelvic bones and a portion of the spinal column would certainly contain its due proportion of the bones of the trunk. From our work it would appear then that the amount of arsenic present in the body at the time of death, calculated as arsenious oxide, was 3.1192 grains. Of this amount 1.007 grain was actually weighed, while nearly half of the total amount was separated and examined.

Among the many peculiar features of these results there is perhaps no one more striking than the irregular distribution of the arsenic in the muscle tissue. The following table, in which the arsenic is calculated in grains per pound of sampled tissue, plainly shows this:

1 lb. sampled	thigh bone	contained	.000	grain	As_2O_3
1 "	leg	"	.011	"	"
1 "	transverse sec.	"	.021	"	"
1 "	arm	"	.034	"	"
1 "	muscle from breast		.087	"	"
1 "	muscle from back		.260	"	"

Now in cases of chronic poisoning, or where persons are habituated to the use of arsenic, the regular distribution of the poison through all parts of the muscle tissue is quite noticeable. Thus in a case previously reported[1] the following results were obtained:

1 lb. sampled	thigh bone	contained	.004	grain	As_2O_3.
1 "	leg	"	.033	"	"
1 "	arm	"	.046	"	"
1 "	transverse sec.	"	.109[2]	"	"
1 "	muscle and ribs, left breast		.063	"	"
1 "	abdominal muscle, right side		.040	"	"

[1] This Journal, **2**, 332.

[2] The increased amount noticed here is undoubtedly due to the fact that the section extended up higher than in the present case; and as the internal organs lay in place in the body for a year and a half, there was undoubtedly more or less diffusion at this point.

In this case, with the exception of the transverse section, the results obtained are within certain limits comparatively constant. There is not that gradual increase from nothing in the bone up to a quarter of a grain per pound in the muscle of the back, as noticed in the case under discussion. This irregular distribution of the poison in tissue of the same kind is certainly indicative of the arsenic having been taken but a short time before death, particularly as in the bone we find none whatever, or at least none in the quantity examined; while, on the other hand, the nearer we approach the great vessels and organs of the body the greater the amount of arsenic in the muscle tissue. The uneven distribution is due, then, presumably to lack of time, while the entire absence of the poison from the portion of bone examined even more strongly excludes the possibility of chronic poisoning.

Again, in cases of chronic poisoning, or where the arsenic has been in the body for some time previous to death, it is customary to find considerable of the poison in the kidneys, since, as is well known, elimination commences very quickly, and continues without interruption until the poison is wholly removed from the body or until death intervenes. In this case, however, the amount of arsenic in both kidneys is but .029 grain, while in the tongue and throat there is nearly three times as much. Once again, the amount of arsenic in the tongue and throat is nearly as much as the amount contained in the entire left arm; results which would hardly be expected in cases where the poison had had sufficient time for even distribution.

In a previous article[1] Johnson and Chittenden called attention to the fact that the form of the poison, viz. whether readily soluble as sodium arsenite, or comparatively insoluble as arsenious oxide, undoubtedly modifies the amount and rate of absorption, particularly by the brain and muscle tissue. This view was based partly on the results obtained by Scolosuboff[2] and by E. Ludwig,[3] and partly on the results of our own toxical examinations and experiments on animals. Thus Scolosuboff, working entirely with sodium arsenite in solution, obtained results all of which agreed in showing that the nerve tissue of the poisoned animal both in acute and chronic cases contains a much larger percentage of arsenic than the muscle tissue

[1] This Journal, **2**, 332.
[2] Bulletin de la Société Chimique de Paris, **24**, 124.
[3] Anzeiger der K. Akad. d. Wissensch. Wien, **18**, 18. See this Journal, **2**, 336–337.

or even the liver. Thus in one experiment the brain of a bull-dog fed on sodium arsenite gave per 100 grams tissue .00885 gram metallic arsenic, while the same weight of liver yielded only .00271 and the muscle but .00025 gram metallic arsenic. Scolosuboff's only error was one of theory, in that he assumed what he had found to be true of sodium arsenite to be true also of the more insoluble arsenious oxide, thus producing much confusion on this point. Again it has been recently asserted, without foundation, that the presence or absence of arsenic in the brain is an index as to whether the poison was introduced into the body before or after death. It is undoubtedly true that the finding of arsenic in the brain is an indication amounting almost to proof that the poison was not *post mortem*, since by no ordinary process of diffusion could the arsenic pass such a distance from the alimentary tract, especially in view of the rapid fixation of the poison by conversion into the insoluble sulphide. But on the other hand, in cases of poisoning with arsenious oxide, the absence of arsenic in detectable quantities in the brain in nowise proves, in the writer's opinion, that the poison was not taken prior to death.

E. Ludwig, of Vienna, from his experience in the examination of human beings poisoned with arsenious oxide, both in acute and chronic cases, as well as from his experiments on dogs, decides that with this form of arsenic the bones and brain contain but a mere trace of the poison, while the liver, as a rule, contains the most arsenic. This view is substantiated by the results from the analysis of the body of Mary Stannard, Mrs. Riddle, and our experiments on animals; for even where large quantities of arsenious oxide have been taken during a period of many days, the amount found in the brain is generally unweighable.

This view being correct, the amount of arsenic found in the brain in the present case admits of but one interpretation. Only one-third of the brain was delivered to the writer for analysis, but this amount contained .025 grain of arsenic, being in the proportion of .034 grain to 1 lb. of brain and alcohol. The only theory then consistent with this result and with the facts at our disposal is that the arsenic was taken in a form readily soluble and diffusible. Again, the large amount of arsenic found in the muscle tissue of the back is not otherwise easily accounted for.

NEW HAVEN, *January* 11, 1883.

HYDRATED CARBON DISULPHIDE.

By F. P. Venable.

This body, discovered by Berthelot[1] and Wartha,[2] has been examined also by Duclaux[3] and by Ballo.[4] The descriptions of it given in our text-books show, however, that our knowledge of it is still somewhat indefinite and incomplete. The following experiments, undertaken at first for the purposes of class illustrations, may serve to clear up some of the doubtful points concerning this body. In filtering carbon disulphide, a sensation of decided cold will be noticed whenever the filter paper is touched. To determine the lowering of temperature caused by the rapid evaporation of the carbon disulphide, a thermometer bulb was wrapped with filter paper, and then suspended over a shallow vessel so that the paper dipped beneath the disulphide contained in it. The mercury sank rapidly to 18° C., and the paper became covered with a peculiar cauliflower-like growth of a snow-white substance, which was seen to be the same as that produced by forcing a current of air across the surface of the disulphide. In further experiments with the thermometer the paper was discarded as uselessly cumbrous, the thermometer was hung just touching the liquid, and evaporation was started by blowing through a tube obliquely into the disulphide so that the little waves struck against the bulb. The formation of the snow-like solid soon commenced. The blowing could then be stopped, and the growth went on rapidly until it had reached a height of 5–6 cm. above the surface. If a current of air was directed upon this growth, it increased most rapidly on the side exposed to the current, forming little tufts resembling miniature, compactly formed, trees, and reaching in some cases a length 7–8 mm. One point observed was that the amount of moisture in the air had a decided effect upon the ease of causing this formation and the rapidity of the growth.

A simple and effective mode of showing as a class experiment the abstraction of heat by the rapid evaporation of the disulphide, or more properly speaking by the formation of the hydrate, is to take a small glass tube with thin walls (such as is used for seed specimens) about 90 mm. long and having a diameter of 10 mm.

[1] Ann. Ch. Phys. [3] **46**, 490.
[2] Bull. Soc. Chim. [2] **8**, 258.
[3] Ber. Chem. Ges. **3**, 80.
[4] Ber. Chem. Ges. **4**, 118, 160, 294.

This tube is provided with a collar of copper wire having two projecting points which turn easily in the ends, bent into rings, of a strong copper wire attached to a support. The ring of one of the ends of the longer and stouter wire should not be closed, so that the tube can be easily unmounted. This arrangement gives stability, and the tube is much easier to tilt than when simply suspended by threads. The tube is wrapped with a single layer of filter paper for two-thirds its length, the paper extending about 1 cm. beyond the closed end. This lower edge dips just beneath the disulphide when the tube is in position. The tube is filled about half or two-thirds full of water, is placed in its swing, and in a few minutes the water will be frozen and will not flow out when the tube is inverted. In one experiment, with the tube arranged as above, the water was frozen within four minutes. The original temperature of the water was 50° C. and the relative humidity of the surrounding atmosphere was 74 per cent.

Experiments were also made testing the use of the disulphide with Daniell's hygrometer. The bulb had best be enveloped in filter paper, though muslin will do. A watch-glass containing 3–4 cc. of the disulphide is supported beneath it so as just to touch it.

Compared with ether, the reduction of temperature is more rapid and a lower temperature can be reached. At the same time the trouble is less, as the watch-glass once properly placed, the apparatus is self-acting. Of course if impure carbon disulphide is used a yellow deposit of sulphur is left, but this does not interfere except in so far as a neat appearance is concerned. The impure disulphide quickly loses its disgusting odor, and as the formation of the hydrate goes on, only an ethereal odor can be detected, freer from the disagreeable sulphur compounds than even the most carefully purified disulphide. Contrary to the experience of Wartha (*loc. cit.*) no ill effects were felt from breathing air filled with this vapor, although remaining sometimes two or three hours near the shallow glasses in which the evaporation was going on. Of course in a very confined space it might become injurious.

Ballo has recorded one or two experiments to prove that this cauliflower-like growth is a hydrate and not solid frozen carbon disulphide. The following experiment confirms his results, and may be regarded, I think, as conclusive of the dependence of this body for its formation upon the moisture of the air. An open-necked bell-jar, ground, greased, and tightly fitting to a ground

glass plate, was provided with a large rubber stopper which was pierced with two holes. Through one of these a calcium chloride tube was inserted, through the other a glass tube with a glass rod working tightly in it and bound to it by means of a piece of rubber tubing so as to be air-tight. The calcium chloride tube was 250 mm. long, and was filled with freshly dried calcium chloride. Inside the bell-jar, a glass acid-holder was filled with fresh concentrated sulphuric acid, and on a triangle placed over it was supported a watch-glass containing carbon disulphide purified by the method of Cloez,[1] and carefully distilled. The glass rod had attached to it by a bit of wax a strip of filter paper 25 mm. broad and 100 mm. long, which had been previously dried in an air-bath for two hours at 100°–105° C. After this was put in the bell-jar, the latter was fitted tightly to the glass plate and the whole allowed to stand about thirty minutes, so that every trace of moisture might be removed from the enclosed air. At the expiration of this time the slip of paper was lowered by the movable rod until it touched the carbon disulphide. The liquid rose rapidly in the pores of the paper, but even after some minutes no sign of the solid incrustations could be seen. As the confined space might have interfered with the evaporation, an aspirator was attached to the calcium chloride tube, but no formation of the solid could be induced. The sulphuric acid was then taken from the jar and water substituted for it. The solid commenced to form almost immediately after the lowering of the paper. The liquid did not rise quite so high as in the first case, and aspirating increased the rate of formation but slightly. If the aspiration was continued until the jar was filled with aqueous vapor, the solid formation suddenly and completely melted away.

Several different ways were tried of forming this hydrate. First, carbon disulphide mixed with about 25 per cent. of water, in a test tube, was placed in a mixture of ice and hydrochloric acid (temperature −23° C.), and for purposes of comparison a tube containing distilled water was placed beside it. The first tube became very milky and turbid, and was frozen to an opaque solid; in the second tube the water remained transparent until completely frozen. A second tube of water and the disulphide was stirred whilst freezing, so as to freeze only on the sides and leave a channel open from bottom to top. All that refused to freeze was poured out, the tube

[1] Comptes rendus, **69**, 1356.

corked and its contents allowed to melt. After melting, a layer of disulphide was observed beneath the water. Of course no great reliance can be placed on such an experiment alone, as the oil may have been mechanically entangled and retained. Again, if a few cc. of carbon disulphide be poured through 2–3 cm. of 90 per cent. alcohol in a tube, the two form clear and distinct layers. Let this tube gently down into a freezing mixture of ice and hydrochloric acid, and the carbon disulphide becomes turbid, while delicate cloud-masses form in the alcohol, and if the alcohol contains more than 10 per cent. water it becames milky and opaque. These cloud-masses disappear above —10° or —9°C., but the temperature could not be accurately fixed, as it seemed to depend upon the amount of carbon disulphide and water held in suspension or solution. If the alcohol and disulphide stand for some time all disulphide apparently settles out, as the cloudiness cannot be again produced by cooling. Care was of course exercised to prevent any agitation or mixing of the liquid layers in sinking the tube into the freezing mixture. A mixture with ether containing a small percentage of water gave also a turbid appearance on being cooled, but the layers were not distinct, nor, on taking the tube from the freezing mixture, did the cloudiness disappear so easily as in the case of the alcohol. Experiments with it then could not be so easily observed nor so rapidly repeated.

The temperature of formation or decomposition given by Wartha (—12° C.) needs additional data to make it correct, according to the following experiments. Even when evaporation and the formation of the hydrate was rapidly going on in a shallow watch glass full of the disulphide, the temperature of the liquid itself did not fall below —6° C. For these experiments a Geissler thermometer graduated to $\frac{1}{10}$ degrees was used, the bulb was nearly spherical, and from its under surface a small bead of glass projected. With this bead touching the surface of the carbon disulphide and the evaporation started by blowing upon it for a short time, the incrustations soon covered the bulb, and the mercury sank rapidly to about —9° C. It then sank very slowly. Seemingly more carbon disulphide was drawn upon the bulb than was used in forming the solid, as the latter had an oily appearance, and this probably tended to keep up the temperature. If the thermometer was raised entirely above the liquid the oily look disappeared, the tufts of solid, before thick and short, branched out and grew stiff and

strong, while the mercury rapidly sank to a constant point. To determine this point then the solid was allowed to form over the bulb and some extra disulphide was taken up. By a crank arrangement the thermometer was then raised several inches above the surface of the liquid, and the lowest temperature reached noted. The stay at this point sometimes lasted one or two minutes before the rapid rise commenced. If the thermometer was blown upon whilst the mercury was sinking, the temperature could be reduced several degrees below the point of decomposition. If the constant point had been reached and the mercury was beginning to rise, even if only $\frac{1}{10}$ degree, blowing caused a very rapid rise and melting of the hydrate. The lowest temperature reached by blowing was —19.5° C., the relative humidity of the room being 75. When the thermometer was wrapped with filter-paper and this dipped in the disulphide, the reduction went on regularly to the constant point of decomposition. The slow sinking at —9° C. was not noticed.

Several observations showed that the reduction was in a measure dependent upon the relative humidity of the surrounding atmosphere. This was determined at each observation of the point of decomposition, but the experiments could not be made accurately enough to deduce any fixed law. Air saturated with moisture gave no hydrate. From this point the temperature of decomposition seemed to sink, the lowest points being reached when the air contained between 70 and 80 per cent. of moisture. Below 60 per cent. the temperature in a number of observations rose once more. Even if the current of air was too slight to affect a small candle flame, it would still show upon the delicate thermometer used—the variations caused being shown by shielding the bulb on one side or the other. Entire surrounding and protection of the bulb interfered with the evaporation, and of course the evaporation itself caused currents. Some other way must then be devised for determining this point. Guarding against draughts as carefully as possible, the determinations made, some twenty-five or thirty in all, ranged from —14° C. to —17° C. No point such as that mentioned by Wartha (—12° C.) to which the mercury would rise and remain constant, was observed, the rise being rapid and regular till the temperature of the room was reached.

Berthelot gives the point of decomposition as about —3° C.

UNIVERSITY OF NORTH CAROLINA, *February* 10, 1883.

AN ISOPICRAMINIC ACID.

By Charles W. Dabney, Jr.

Some investigations starting from α-metanitrosalicylic acid have led me unexpectedly to an isomer of the well-known picraminic acid.[1] Before entering into the details of the preparation of this new acid and its derivatives, it is necessary to notice the steps by which we have reached the adopted view of the constitution of picraminic acid.

In the first place, picric acid is diorthonitro-paranitro-phenol, counting from hydroxyl as I. This is evident from the fact that it can be produced by nitrating either α-, or orthoparanitrophenol, or β-, otherwise known as diorthonitrophenol.[2]

Secondly, we find that the amido group in picraminic acid is derived from one of the orthonitro groups and not from the paranitro group. Stuckenberg[3] obtained, by nitrating benzoyl-α-amidonitrophenol, derived from paranitroorthoamidophenol, a dinitrobenzoylamidophenol. Stünkel[4] produced independently, by nitrating benzoylorthoamidophenol similarly, a dinitrobenzoylamidophenol, which he proved to be identical with Stuckenberg's phenol. They both gave, by splitting off the benzoyl group, the well-known picraminic acid. Stünkel went further then, and, by getting rid of the amido group in his picraminic acid thus produced by Griess's diazo-reaction, produced again α-dinitrophenol[5] mentioned above, thus putting the question of the constitution of picraminic acid beyond a doubt. Numerous lines of reasoning will lead us to the same constitutional formula, but they are all similar to the argument here cited. Only one other will be mentioned which is entirely different from these.

It is well known that an anhydro compound can only result when the amido group stands in the ortho position, that is,

[1] The literature of picraminic acid can be briefly given. It was first examined by Wöhler, who produced it by reducing picric acid with ferrous oxide (Pogg. Ann. **12**, 488). Berzelius named it from its color *haematinsalpetersaüre* (Jahr. Ber. **9**, 245). Riecker made the acid by reducing picric acid with hydrogen sulphide, and Girard examined it carefully and called it picraminic acid (Berzelius Lehrb. **4**, 677, and Compt. rend. **36**, 421). Gerhardt suggested first, in his Lehrbuch (**3**, 52), that this was identical with *haematinsalpetersaüre*, and Pugh (Ann. Chem. **96**, 83) and Girard (Compt. rend. **42**, 59) established this as the fact about the same time.

[2] Laurent, Ann. der Chemie, **43**, 219.

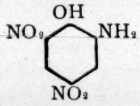
[3] Ber. der deutsch. chem. Gesellsch. **10**, 382.

[4] Dissertat. Göttingen, 1880, 15.

[5] Griess had made this from picraminic acid prepared in the ordinary way. Ann. **113**, 210.

adjoining the OH group. Now, Haarhaus[1] has produced a benzoylpicraminic acid, and made from this, by separating one molecule of water, an anhydro compound, dinitroanhydrobenzoylamidophenol. Stünkel[2] prepared the same from his benzoylpicraminic acid, made, as we saw, from orthoamidophenol.

We may regard the constitution of the picraminic acid molecule thus as as well understood as that of any molecule of this complexity in organic chemistry. It is represented in graphical formula thus:



Prof. Hübner suggested to me at Göttingen in the spring of 1879 to try to introduce a benzoyl group (—COC_6H_5) into α-metamidosalicylic acid (C_6H_3COOH, OH, NH_2, HCl), and then to nitrate the product. The suggestion led to the investigations here reported, although the result was entirely different from what was expected.

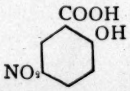
α-Metanitrosalicylic Acid.—A large amount of this acid was prepared by nitrating salicylic acid according to the method of Hübner.[3] The two nitro acids which are made together by this method were carefully separated. I found the quickest way to accomplish this was to combine the two methods proposed by Hübner. A partial separation was accomplished, handling the isomeric acids in great bulk, by repeatedly dissolving in warm water, in considerably more than the amount necessary to dissolve, and subjecting the solution to a winter's cold. The α-nitro acid is considerably less soluble in water below the freezing point than the β-nitro acid. Two lots of acids accumulate thus, a dry mass, chiefly α-acid, and a liquor, chiefly β-acid. Both are converted into their barium salts. Barium β-nitrosalicylate is much less soluble in water than the α-nitrosalicylate. The dry mass of α-acid yields, when converted into barium salts, one small crop of barium β-nitrosalicylate crystals, and then only the α-nitro salt which is pure when it has been crystallized over twice. The liquor yields several large crops of barium β-nitrosalicylate crystals, and finally, upon close concentration, the beautiful bundles of small straw-

[1] Dissertat. Göttingen, 1880, 22. [2] *Loc. cit.* [3] Ann. der Chem. **195**, 7.

yellow crystals of barium *α*-metanitrosalicylate. This salt yielded me the absolutely pure *α*-metanitrosalicylic acid (melting point 228° C.), which was the starting point for these investigations.

The argument for the constitution of this acid is as follows: Kruse[1] obtained from this acid, which is a metanitrohydroxybenzoic acid, as related to benzoic acid, a metanitroorthoamidobenzoic acid, by transforming the OH group into an NH_2 group by means of a well-known reaction. This he then, by getting rid of the NH_2 group (diazo reaction), converted into the familiar metanitrobenzoic acid (melting point 142° C.). It follows from this that the —COOH group and the NO_2 group must stand in the meta relation to each other in the acid under consideration.

As regards the relation of the OH group and the NO_2 group, Hall's[2] work in removing CO_2 from *α*-metanitrosalicylic acid and producing thereby paranitrophenol (melting point 114° C.), puts this beyond question. They are in the para relation. From these considerations it follows that the —COOH and —OH groups are in the ortho position to each other. This has been verified[3] also by the preparation of salicylic acid or hydroxybenzoic acid by converting the NH_2 in anthranilic acid or orthoamidobenzoic acid into — OH. The acid under examination is, therefore, a metanitroorthohydroxybenzoic acid, and indeed that particular metanitro acid in which the nitro group stands in the para relation to hydroxyl, and which has been called accordingly *α*-metanitrosalicylic acid. The graphical formula is:



α-Metamidosalicylic Acid.—The amido acid was prepared from the nitro acid by reducing with tin and hydrochloric acid, according to the method described by Schmitt.[4] The amido acid was only fairly stable when hydrochloric acid was left combined with it, C_6H_3, COOH, OH, NH_2. HCl. The free amido acid decomposed almost immediately. Even the solutions of this hydrochloride had to be handled with extreme care. When they had to

[1] Dissertat. Göttingen, 1877.
[2] Dissertat. Göttingen, 1875. See also Ann. Chem. **195**, 21-30.
[3] Ann. Chem. **149**, 146.
[4] Zeitschr. für Chemie, 1864, 325.

be evaporated a current of hydrogen sulphide was found to check the destructive oxidation somewhat. α-Metamidosalicylic acid hydrochloride crystallizes in beautiful, long, colorless, glassy-looking needles. They were often obtained an inch long, but were very difficult to get perfectly colorless, being generally brownish, with a film of the oxidation products. Upon heating it decomposes rapidly.

Introduction of the Benzoyl Group.—The amido acid just described, thoroughly dried and finely ground, was heated with the weighed amount of benzoyl chloride (boiling point 199°C.), counting molecule to molecule, in a flask fitted with a cork and a long tube. Care was taken to banish every trace of water from the apparatus. As the temperature had to be carefully regulated, the flask was heated in a paraffin bath.

The evolution of hydrochloric acids begins as soon as the bath has reached a temperature of 130° C., showing that a reaction is taking place. Conducted at this temperature, the chief product is the compound designated B farther on. In order to get the largest return of the compound desired for the later work—called C below—it was found necessary to heat the bath up to 170–180° C. and maintain it at this for three hours. The mass melts down to a thin liquid and the evolution of hydrochloric acid ceases.

If the bath is heated up to 200° C. or over, the compound formed in largest amount is the one called A below.

I always found a considerable part of the amido acid and benzoyl chloride unchanged, however the mass was treated. Petroleum oils of various densities, chloroform and various other solvents were tried, heating in a sealed tube, without getting any better results. The three compounds A, B and C were formed in every case, although the amounts of each that were formed differed with the temperature at which the reaction was carried out as already indicated.

After a great deal of work I settled upon the following as the best means of separating these three products. The doughy mass was kneaded and washed under hot water until the benzoyl chloride remaining in it was all decomposed and the benzoic acid removed in great part. All of the new compounds are almost completely insoluble in water. In order to get rid of the last of the benzoic acid it was necessary to dissolve the mass in strong acetic acid, precipitate with much hot water and then wash again. The curdy

white mass that is left is then dissolved in a warm solution of barium hydrate. The pinkish solution is filtered, and carbon dioxide, free from every trace of mineral acid, is passed through it when cooled. The compound A is precipitated along with the barium carbonate. It is washed first with water, then with dilute acid until the barium is all dissolved out, and can be farther purified by dissolving again in the alkaline solution, precipitating with carbonic acid, etc.

The filtrate contains the barium salts of the compounds B and C. Of these two, the C salt is the less soluble in water, and they can be separated by crystallizing the C salt over and over until it appears in large warty aggregations of short white needles. This salt yields the C acid in a pure form. But the separation can be accomplished quicker by throwing down the acids in the filtrate from the A compound and barium carbonate, with hydrochloric acid, and treating the flocculent precipitate after it has been washed and dried with chloroform. The chloroform dissolves the compound B, and leaves the compound C nearly all behind.

The compounds A, B and C are all alike in being amorphous, or only cryptocrystalline, white substances, and in being little soluble in water. They all dissolve very easily in alcohol. They dissolve easily in acetic acid, though in different amounts. But they leave only a crust or scale when the solvent is removed.

The Compound A only forms salts with an excess of strong alkali. Carbonic acid precipitates it from such solutions. Heated up above 250° C., it turns brown and chars gradually. As I have not been able so far to obtain this compound in a pure form, it was impossible to examine it further. We may have here a mixture of compounds.

The Compound B shows a little more tendency to crystallize. When its chloroform solution is evaporated, it separates in little white grains. After passing through the chloroform solution a number of times it melted regularly and suddenly just when 210° C. was reached. It forms a barium salt which is very soluble in water and does not crystallize well. Treated with strong nitric acid this compound gives a handsome nitro compound. A further notice of this is postponed until it can be more thoroughly examined.

Compound C, α-Benzoylamidosalicylic Acid.—$C_6H_3COOH, OH, NHCOC_6H_5$. Melting point 252° C. The third compound is, as we shall see, the amido acid to which one benzoyl group ($-COC_6H_5$) has been added. Its behavior renders it very probable that its

formula is C_6H_2, COOH, OH, $NHCOC_6H_5$ and not C_6H_3COOH, $OCOC_6H_5$, NH_2. The acid is very little soluble in hot water, very easily soluble in pure acetic acid, insoluble in chloroform, benzol and gasoline or naphtha. It was not crystallized. The pure acid, obtained from the barium salt, came down as a white powder from its solution in acetic acid, as this evaporated over caustic potash under a bell-glass. This powder was only cryptocrystalline at best. It melts at 252° C., and forms immediately a dark, tarry-looking liquid. Strong alkalies decompose the solutions of its salts when warm, and cause brown flocculent masses to appear.

Analyses.

Carbon and Hydrogen.—I. 0.3231 gram of the acid, separated out of the pure barium salt and dried over sulphuric acid, gave 0.7693 gram carbon dioxide, equal to 0.2098 gram carbon; and 0.1358 gram H_2O, equal to 0.015088 gram hydrogen.

II. 0.3914 gram of the same acid, which was thrown down from the acetic acid solution in addition, gave 0.9429 gram CO_2, equal to 0.25715 gram carbon; and 0.1655 gram H_2O, equal to 0.018388 gram hydrogen.

Nitrogen.—0.2790 gram of the acid, from the barium salt directly, gave 14.0 cc. nitrogen at 15° C. and 735 mm., equal to 0.015849 gram nitrogen.

	Calculated for C_6H_2, COOH, OH, $NHCOC_6H_5$.		Found. I.		II.	
C_{14}	= 168 =	65.36 per ct.	64.93 per ct.	65.70 per ct.	...	
H_{11}	= 11 =	4.28 "	4.67 "	4.70 "	...	
N	= 14 =	5.44 "	... "	...	5.66 per ct.	
O_4	= 64 =	24.92 "	... "	...	... "	

Salts.—*a*-Benzoylmetamidosalicylic acid is a rather strong acid. It would appear from the formula adopted that it is a dibasic acid. The H of hydroxyl and the H of carboxyl might both be substituted by a metal. But its behavior indicates that the second metal atom is at least not stable in the presence of carbonic acid. The only crystallizable salts are those in which *one* H atom is substituted by a metal. When barium hydrate solution is added to a concentrated solution of the monobasic salt, a heavy white precipitate is formed which could not be obtained crystallized. Only the monobasic barium and calcium salts were obtained in sufficiently

well-defined form for analysis. The metal salts were all gelatinous precipitates. The copper salt was a light blue-colored jelly; the zinc salt a transparent jelly, etc. The salts of potash and soda were only obtained as a transparent glassy crust when their solutions were evaporated down.

Barium α-benzoylmetamidosalicylate.

$(C_6H_3, OHNHCOC_6H_5, COO)_2Ba + 6H_2O$. This salt is formed when the acid is dissolved in a solution of barium hydrate, and, more slowly, when the acid is boiled in water with barium carbonate. A pinkish solution is formed which deposits brown flocculent masses on evaporation. This brown oxidation's product renders the salt brown or pink at first, but after frequent crystallizations it is obtained in small colorless needles, which group themselves together in large wart-like masses; very easily soluble in water, stable in the air at ordinary temperatures and over sulphuric acid, but loses its water very easily on heating.

Water.—I. 0.5540 gram of the air-dry salt lost only a trace of water over sulphuric acid. Heated up to 120° C. it lost nearly all of its water. Heated continuously at 140° C. it was constant. 0.0810 gram H_2O lost, equal to 14.62 per cent.

II. 0.9508 gram of the air-dry salt lost up to 160° C. 0.1378 gram water, equal to 14.49 per cent.

Calculated for $(C_6H_3,OH,NHCOC_6H_5,COO)_2Ba+6H_2O$.	Found. I.	II.
H_2O = 14.22 per cent.	14.62 per cent.	14.49 per cent.

Barium.—I. 0.4268 gram of the water-free salt gave 0.0870 gram $BaSO_4$, equal to 21.01 per cent. barium.

II. 0.6293 gram of the water-free salt gave 0.2282 $BaSO_4$, equal to 21.28 per cent. barium.

Calculated for $(C_6H_3,OH,NHCOC_6H_5COO)_2Ba$.	Found. I.	II.
Ba = 21.10 per cent.	21.01 per cent.	21.28 per cent.

Calcium α-benzoylmetamidosalicylate.

$(C_6H_3, OH.NHCOC_6H_5, COO)_2Ca$. This salt is formed in similar manner as the barium salt. As the warm concentrated solution cools down, the very soluble, little, blunt needles crystallized out. They have a fine satin lustre when dry.

Water?—0.5058 gram of the air-dry salt lost, under a bell glass over strong sulphuric acid, 0.0020 gram only, and heated up to 170° C. it lost in weight only 0.0035 gram more. Whether the salt loses all of its water of crystallization in the process of removing the moisture (lying on porous paper in the atmosphere of a heated room), or whether it has *no* water of crystallization, could not be decided. The salt did not appear to change in any respect from the moment the adhering water was removed.

Calcium.—I. 0.1958 gram of the salt, dried at 170° C., gave 0.0480 gram calcium sulphate, equal to 7.18 per cent. calcium.

II. 0.2104 gram of the air-dried salt gave 0.0512 gram calcium sulphate, equal to 7.12 per cent. calcium.

Calculated for $(C_6H_3, OH, NHCOC_6H_5, COO)_2Ca$.	Found. I.	II.
Ca = 7.24 per cent.	7.18 per cent.	7.12 per cent.

The behavior of this acid when treated with nitric acid renders it almost certain, as we shall see, that its constitution is as written above. Just three different compounds are conceivable as resulting immediately from the entrance of the benzoyl group into α-metamidosalicylic acid.

(1) The acid we have just described agrees with the formula C_6H_3, OH, $NHCOC_6H_5$, COOH. (Compound C.)

(2) C_6H_3, $OCOC_6H_5$, NH_2, COOH.

(3) $C_6H_3OCOC_6H_5$, $NHCOC_6H_5$, COOH. The compounds A and B, mentioned above, may correspond to the formulas (2) and (3). This remains to be ascertained.

Treatment of α-Benzoylmetamidosalicylic Acid with Nitric Acid, Benzoylparamidodinitrophenol. — C_6H_2OH, $(NO_2)_2NHCOC_6H_5$. Melting point 250° C. Considerable difficulty was experienced at first in the effort to nitrate the benzoylamido acid just described. When it was carried into fuming nitric acid at ordinary temperatures a violent reaction took place, the compound was completely broken up, a large amount of gases given off and the liquid heated. A variety of methods for moderating the reaction were tried. The following were reasonably successful.

I. Into a mixture of equal parts of concentrated nitric and acetic acids, cooled down to 0° C., small portions of the powdered compound were slowly carried. This would go on for a short time, the compound dissolving in the mixture, until suddenly the mixture

would get red, the temperature rise considerably, and gases come off freely. The mixture had to be thrown, immediately at this point, into ice-cold water. If allowed to stand the temperature would continue to rise and the compound would be entirely destroyed, as in the first instance. It was impossible to stop the reaction exactly at the right point, even under these conditions. A considerable amount of picric acid was always found among the products. The nitro compound appeared in the cold water as a bulky, flocculent, yellow precipitate. The aggregate of nitro product by this method was so unsatisfactory that I sought a better method.

II. I obtained a much larger amount of the desired compound, though still far less than the calculated amount, when α-benzoyl-metamidosalicylic acid was dissolved in 20 or 30 times its weight of acetic acid, four or five drops of nitric acid were added to each 100 cc. and the mixture warmed to about 80° C. As soon as the proper temperature was reached the liquid became suddenly a beautiful light yellow color. It was then immediately thrown into about four times its volume of water; otherwise a decomposition set in. Sometimes some unchanged amido acid appeared alongside of the nitro product.

The nitro compound crystallizes well out of alcohol and is easily purified. It is a handsome compound, crystallizing in glistening yellow plates. Heated up above 150° C. it gives off red vapors and then melts at 250° C.

It is easily soluble in strong acetic acid, somewhat less in alcohol, still less in benzol and naphtha, and very little soluble in water.

ANALYSES.—*Carbon and Hydrogen.*

0.2385 gram of this nitro compound separated from its well-crystallized barium salt, recrystallized out of the alcohol solution and thoroughly dried, gave 0.4522 gram CO_2, equal to 0.12332 gram carbon; and 0.0765 gram water, equal to 0.00850 gram hydrogen.

Nitrogen.—I. 0.3552 gram same compound gave 44 cc. of nitrogen at 14° C. and 735 mm., equal to 0.050041 gram nitrogen.

II. 0.1700 gram from another nitration, purified in the same way gave 20.2 cc. nitrogen at 15° C. and 734 mm., equal to 0.022836 gram nitrogen.

	Calculated for $C_6H_2, OH, (NO_2)_2NHCOC_6H_5$.		Found. I.	II.
C_{13}	= 156 = 51.49 per ct.	51.70 per ct.	...	...
H_9	= 9 = 2.97 "	3.56 "	...	...
O_6	= 96 = 31.68 "	...	...	...
N_3	= 42 = 13.86 "	...	14.08 per ct.	13.42 per ct.

The compound first expected was a nitro-benzoylamidosalicylic acid. Calculated for this :

C_6H_2, OH, NO_2, $NHCOC_6H_5$, COOH.

C_{14}	= 168 = 55.62	per cent.
H_{10}	= 10 = 3.31	"
N_2	= 28 = 9.27	"
O_6	= 96 = 31.80	"

The nitro compound examined turns out to be a dinitrobenzoylamidophenol, instead of the mononitrocarboxylphenol which we look for. The —COOH group and one H atom have been driven out of the compound by the nitration and two —NO_2 groups have entered into it in their place. I failed to find anything in the various mother-liquors which were examined, except some benzoic acid and a little picric acid, which undoubtedly resulted from the decomposition of the compounds.

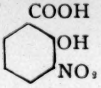
A large variety of methods were tried, without success, in the effort to find the conditions under which a mononitrocarboxyl acid would be formed. I always obtained, when there was any reaction at all, the dinitrophenol just described, and this alone. The great ease with which this reaction takes place renders it improbable that any other product can be obtained from *α*-benzoylmetamidosalicylic acid and nitric acid.

I may instance one attempt. Three or four drops of nitric acid were added to about 50 cc. of concentrated acetic acid, in which a little of the benzoylamido acid had been dissolved, and the open beaker was put under a bell-glass over caustic potash until the whole had dried up. Although the largest portion of the amido acid remained unchanged, some of the dinitrophenol was formed and nothing else.

The expulsion of the carboxyl group is a frequent occurrence under these circumstances. A number of cases where it has occurred in compounds similar to this could be cited. Hübner and Babcock[1] note it in the case of a compound closely allied to

[1] Ber. d. deutsch. chem. Gesell. **12**, 1346.

our benzoylmetamidosalicylic acid. By the nitration of β-metanitrosalicylic acid, β-dinitrophenol (melting point 63°–64° C.) was always produced alongside of dinitrosalicylic acid. In their case



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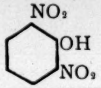
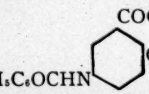


In our case



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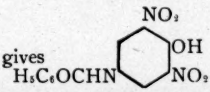


The —OH group determines the location of the entering negative groups in both these cases, as usual, and in both products we find a carboxyl group replaced by a nitro group.

Salts.—Benzoylparamidodinitrophenol appears to be a fairly strong acid, and forms stable and, in the main, finely crystallizable salts. The solutions of its salts are all deep bluish red All of the salts have a rich gold-like lustre. The salts of the alkalies and alkaline earths crystallize especially well. Besides these described below, I have formed a zinc salt, which crystallizes in blunt, bright red needles, and is very soluble in water, and a silver salt, which crystallizes in wartlike masses made up of very small reddish-yellow needles, which are much less soluble.

The Potassium Salt, $C_6H_2(NO_2)_2$, $NHCOC_6H_5$, $OK.HO_2$. This salt was obtained by warming the phenol with a solution of pure potassium carbonate. The salt is very soluble in water. It is less soluble in dilute alcohol, and can be more readily crystallized from this. It forms handsome light red needles, with a splendid golden yellow lustre. The water-free salt is a dark brick-red color.

Analysis.

Water.—0.5336 gram of the air-dried salt lost very slowly up to 180° C. 0.0280 gram water and then remained constant.

Calculated for $C_6H_2(NO_2)_2$, $NHCOC_6H_5$, $OK.H_2O$.	Found.
Water = 5.04 per cent.	5.24 per cent.

Potassium.—0.5056 gram of the water-free salt gave 0.1320 gram potassium sulphate, equal to 0.05924 gram potassium.

Calculated for C_6H_2, $(NO_2)_2$, $NHCOC_6H_5$, OK.	Found.
K = 11.46 per cent.	11.71 per cent.

The Barium Salt, $(C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2Ba \cdot 3H_2O$. When the phenol is boiled with barium carbonate a deep bluish red solution is formed. This is filtered off and allowed to cool, when the fine, bright red needles of the barium salt usually appear at once. The salt is perfectly pure after being recrystallized twice. It has the same brilliant yellow lustre as the potassium salt, although not quite so bright. The water-free salt is a dark dead red.

ANALYSIS.

Water.—0.5336 gram of the air-dry salt lost at 210° C. all of its water, 0.0365 gram. The salt loses its water with difficulty.

Calculated for C_6H_2, $(NO_2)_2$, $NHCOC_6H_5$, $O)_2$ Ba. $3H_2O$.	Found.
H_2O = 6.79 per cent.	6.82 per cent.

Barium.—I. 0.3256 gram of the water-free salt gave (the phenol precipitated and filtered off, and the barium determined in the filtrate), 0.1011 gram barium sulphate, equivalent to 0.059446 gram barium.

II. 0.1646 gram of the water-free salt gave (heated with H_2SO_4 until all of the organic matter was driven off), 0.0522 gram of barium sulphate, corresponding to 0.030693 gram barium.

Calculated for $(C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2$ Ba.	Found. I.	Found. II.
Ba = 18.49 per cent.	18.25 per cent.	18.64 per cent.

The Calcium Salt, $(C_6H_2,(NO_2)_2,NHCOC_6H_5, O)_2Ca.\ 4\frac{1}{2}H_2O$, was produced in similar manner to the barium salt. It crystallizes in glistening, yellowish-red scales or plates, which are quite soluble in water.

ANALYSIS.

Water.—0.4266 gram air-dry salt lost, at 200° C. heated, 0.0478 gram water, and remained constant.

Calculated for $(C_6H_2(NO_2)_2, NHCOC_6H_5, O)_2Ca.4\frac{1}{2}H_2O$.	Found.
H_2O = 11.17 per cent.	11.20 per cent.

Calcium.—0.3788 gram water-free salt gave 0.0840 gram calcium sulphate, corresponding to 0.02461 gram calcium.

Calculated for $(C_6H_2(NO_2)_2NHCOC_6H_5O)_2Ca$.	Found.
Ca = 6.20 per cent.	6.49 per cent.

The Lead Salt, $(C_6H_3(NO_2)_2NHCOC_6H_5, O)_2Pb$. Anhydric? This salt was precipitated when acetate of lead was added to a concentrated hot solution of the pure potassium salt. It forms a dark red crystalline mass, which dissolves in much warm water.

ANALYSIS.

Water.—Heated up to 180° C. it lost very little in weight, and did not change at all in appearance as did the other salts on heating.

Lead.—0.3520 gram dry salt gave 0.1290 gram lead sulphate, corresponding to 0.0886 gram lead.

Calculated for $(C_6H_2, (NO_2)_2, NHCOC_6H_5, O)_2Pb$.	Found.
Pb = 25.49 per cent.	25.17 per cent.

It follows from these analyses that this nitro compound obtained as described from *a*-benzoylamidosalicylic acid, has the general formula $C_{13}H_9N_3O_6$. We have already referred to the ground for believing that at least one NO_2 group has fastened upon the phenol group. The removal of the COOH group in the nitration renders this much very probable. But the other NO_2 group may be fastened upon the benzoyl group ($—COC_6H_5$) and the rational formula may be C_6H_2, OH, NO_2, $NHCOC_6H_4NO_2$. Such a compound is known. Güssefeld[1] has produced from other material the very phenol which might be expected here, and has established its constitution. By nitrating benzoylparamidophenol (the amido group in the same position as in our phenol) with concentrated nitric acid, he produced a dinitro compound with the same general formula as our phenol. By splitting off from this a well-known nitrobenzoic acid (C_6H_4, NO_2, COOH), he showed, however, that his compound was a nitrobenzoyl-paramidonitrophenol. That is, Güssefeld found that

C_6H_4, OH, $NHCOC_6H_5$ (para) (melting point 227.5° C.) gave C_6H_4, OH, NO_2, $NHCOC_6H_4$, NO_2.

While I claim that C_6H_3, OH, COOH, $NHCOC_6H_5$ (para) produces C_6H_2OH, NO_2, NO_2, $NHCOC_6H_5$.

A comparison of the properties of these compounds sustains the opinion that they are different bodies. The solubilities are entirely different. Güssefeld's compound is, for example, dissolved in alcohol only in traces, and is very difficultly soluble in concen-

[1] Dissertat. Göttingen, 1880.

trated acetic acid. His dinitro product melts at 225° C., my product at 250° C., etc. Sharper distinctions than these were hardly possible. The following investigations put this hypothesis about the constitution of the molecule of our dinitrophenol entirely beyond doubt:

Decomposition of Benzoyl-paramidodinitrophenol with Hydrochloric Acid.

About one gram of the dinitrophenol was heated in a sealed tube with 5 cc. of concentrated hydrochloric acid and 3 cc. of water to 130° C. for about twelve hours. The phenol was completely dissolved. Upon cooling a bulky crystalline mass separated out.

Benzoic Acid.—The solid part was filtered off, washed with a little cold water, and recrystallized by dissolving in hot water and letting cool. The crystals continuing to have a yellow color, they were boiled with barium carbonate and the filtrate evaporated down closely. The little scales which crystallized out were yellowish at first, but after recrystallization they were entirely colorless. Small, glistening scales or plates, very soluble in water. The acid obtained from this salt crystallized in shining white, flat needles or plates, somewhat flexible. Melting point 118°—119° C. The unmistakable odor of benzoic acid. The acid was compared as to solubility, etc., with benzoic acid produced in the ordinary way. The melting point of benzoic acid is given in the books at 120° C., but none I could get melted higher than 119° C. The barium salts were compared also. There could be no doubt about this product being benzoic acid.

Diorthonitroparamidophenol or Isopicraminic Acid (melting point 170° C.)

The yellow filtrate was evaporated to dryness. The reddish brown crust which remained was washed with cold water and then dissolved in hot water. As the rather concentrated solution became cool, suddenly a lot of beautiful little needles separated out. Upon recrystallization, fine, long, thin crystals were obtained. In the liquid, and while still wet, they shone like gold. Dried in the air on porous paper the crystals lost this beautiful lustre and became a dead brownish yellow. This appeared to be due to the formation of just the thinnest film of some oxidation product over their surface. The large crystals, which appear to the naked eye

to be individual needles, were resolved, under the microscope, into bundles of exceedingly fine, delicate little needles.

The compound dissolves very easily in alcohol; in benzol and naphtha less easily. It is very little soluble in cold water, but easily in hot. The finest crystals were obtained from the water solution. The solution in benzol yields yellowish-brown bundles of needles; in chloroform coarser dark brown needles, which approach nearer to plates in shape. All of these solutions are of a beautiful cherry-red color. Very dilute solutions have a delicate rose tint. Crystallized from these various solutions, the compound melted uniformly, after the fine large crystals had been once obtained, at 170° C. It appeared to decompose as it melted. Allowed to cool and heated a second time it always melted much lower.

The compound appeared to combine with strong acids, like hydrochloric, dissolving in them to form light yellow solutions. The acid probably unites with the amido group in the compounds, but the resulting compound could not be obtained separate from the liquid. The compound unites with alkalies to form well-crystallized, handsome salts, all of whose solutions have a fine, deep bluish red color, nearly the same tints, but much darker than the solutions of the free compound.

Analysis.

Hydrogen and Carbon.—0.2832 gram of the compound, dried over H_2SO_4, was burned with oxide of copper and gave 0.3720 gram CO_2, corresponding to 0.10145 gram carbon and 0.0664 gram H_2O, corresponding to 0.007377 gram hydrogen.

Nitrogen.—0.1485 gram of the air-dry compound gave 27.7 cc. of nitrogen, measured at 24° C. and 749 mm., corresponding to 0.030608 gram nitrogen.

Calculated for $C_6H_2OH,(NO_2)_2,NH_2$.	Found.
C = 36.13 per cent.	35.82 per cent.
H = 2.51 "	2.60 "
N = 21.10 "	20.60 "

Salts.—The salts of the alkalies have been mentioned. I lost a good deal of material in trying to get salts of barium and calcium. They did not crystallize at all well, and I have not, so far, been able to get them sufficiently pure for analysis. This compound and its salts explode pretty sharply when strongly heated. This

property, which it was difficult to avoid, caused me to lose several analyses. This explains how it is that I have no more analyses of the original compound and its salts to present at this time.

The Potassium Salt.—$C_6H_2(NO_2)_2NH_2OK$.

This was formed by bringing together the weighed amount of potassium carbonate and the phenol in warm water. The compound is a rather strong acid and attacks the carbonates in the cold. A beautiful bluish-red solution is at once formed. The salt is so very soluble in water that I could not get good crystals from this solution. It was evaporated to dryness and the residue dissolved in alcohol. The salt crystallizes from this solution in bluish-black needles.

Water?—The salt which had been dried over sulphuric acid was heated up to 130° C. without losing appreciably in weight.

Potassium determination.—After several vain attempts, a determination of potassium as the sulphate was obtained, as follows: The powdered salt was weighed out into a platinum crucible. A little concentrated sulphuric acid was added, and it was warmed very gently for a considerable time, until all of the salt was decomposed and the nitro compound had been quietly but completely broken up by the acid. It was then strongly heated and a perfectly pure sulphate obtained. 0.1948 gram of the salt dried at 130° C. gave 0.0760 gram of potassium sulphate, corresponding to 0.034124 gram potassium.

Calculated for $C_6H_2, (NO_2)_2, NH_2, OK$.	Found.
K = 16.9 per cent.	17.5 per cent.

From these analyses it is sufficiently evident that we have here a dinitroamidophenol or a compound with the picraminic acid formula. In agreement with our preconceived opinion, based upon a comparison of the last compound with Güssefeld's compound, it is now proved that both of the nitro groups went into the phenol. We get, by splitting, the well-known benzoic acid and a dinitro compound.

Picraminic acid was prepared in the usual way and compared carefully with the isopicraminic acid. Ordinary picraminic acid crystallizes from water in orange-red needles, which melt at 165° C. The solubilities are very different. 100 parts of water at 22° C.

were found to dissolve 0.140 part of picraminic acid and only 0.082 part of the new acid. Picraminic acid is very little more soluble in hot than in cold water, while 100 parts of hot water (just under boiling) dissolve 0.812 part of the new picraminic acid. The potassium salts were compared also. For details see the table.

If this is an isopicraminic acid, the compound from which it was obtained was simply a benzoyl-isopicraminic acid, and the comparison of this with the benzoyl derivative of the ordinary picraminic acid, which has been produced from various materials and studied by several chemists, yields us another strong argument for the proposition that this is a case of isomerism and not one of identity.

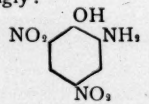
Stuckenberg[1] obtained, as we saw in the beginning, by nitrating benzoyl *a*-amidonitrophenol, a benzoylamidodinitrophenol. This he describes as crystallizing in greenish-yellow needles and as melting at 218–219° C. Haarhaus[2] obtained a compound of similar composition from picraminic acid itself, which he describes in like terms. Lastly, Stünkel[3] produced a dinitro-benzoylamidophenol by nitrating benzoylorthoamidophenol, from which he then procured the old picraminic acid in a way exactly parallel to the method in which I have prepared isopicraminic acid from my dinitro-benzoylamidophenol. He describes his dinitro product as crystallizing in greenish-yellow needles and having a melting point 220° C. My dinitrobenzoylamidophenol crystallizes in glistening yellow plates and melts, decomposing at the same time, at 250° C.

Through the courtesy of Dr. Stünkel in putting portions of his original preparations at my disposal, I was enabled to make myself a thorough comparison of these two benzoyl derivatives of the two isomeric acids and their salts. The differences are very marked all the way through. The salts of the longer-known phenol are all of a lighter yellow color and less lustrous than the salts of the new phenol. The latter are characterized by a more decided red color. The differences between the barium salts are otherwise quite distinct. The water of crystallization is different. The barium salt of the older phenol is very difficultly soluble in water, while the salt of the newer is easily soluble. Further details will be found in the table.

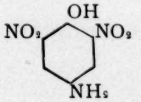
[1] *Loc. cit.* [2] *Loc. cit.* [3] *Loc. cit.*

The isomerism is readily explained when we consider the constitution of the material from which the isopicraminic acid was derived. The amido group in ordinary picraminic acid stands, as as we saw, in the ortho position. In the acid from which we started it stands, as we found, in the para position to hydroxyl (meta to carboxyl). If a transposition of the groups has not taken place then—and this is hardly conceivable in the case of a nitration taking place so very easily and at so slow a temperature as ours did—the resulting dinitroamidophenol must necessarily be isomeric and not identical with the known dinitroamidophenol or picraminic acid.

The graphical formulas of the two picraminic acids must be accordingly:



Orthoamidodinitrophenol or Picraminic acid.



Paramidodinitrophenol or Isopicraminic acid.

Comparison of Picraminic Acid, Isopicraminic Acid, and their Derivatives.

Picraminic Acid or Ortho-amidodinitrophenol. — $C_6H_2OH(NO)_2NH_2$. Melting point 165° C. Crystallizes from water in orange-red needles, from chloroform in blood-red scales. Soluble in alcohol, little in water, hot or cold. Solutions an orange-red color.[1]

Potassium Salt.—$C_6H_2(NO_2)_2NH_2OK$. Red, translucent rhombish plates, which are rather soluble in water, but little soluble in alcohol. Explodes on heating strongly.[1]

Isopicraminic Acid or Para-amidodinitrophenol. — $C_6H_2OH,(NO_2)_2NH_2$. Melting point 170° C. Crystallizes from water in bundles of exceedingly fine needles, having a golden lustre when wet, brownish yellow when dry. Very easily soluble in alcohol, easily soluble in warm water, very little in cold. Solutions bluish red.

Potassium Salt.—$C_6H_2(NO_2)_2NH_2OK$. Bluish-black needles. Extremely soluble in water, less in alcohol. Explodes sharply when strongly heated.

[1] Girard, Jour. flir pract. Chem. **59**, 142, and Compt. rend. **36**, 421.

Benzoylorthoamidodinitrophenol, or Benzoylpicraminic Acid. C_6H_2OH, $(NO_2)_2NHCOC_6H_5$ (ortho). Melting point 220° C.[1] Greenish-yellow needles, difficultly soluble in warm concentrated acetic acid, still more difficultly in alcohol and benzol, almost completely insoluble in water (Stünkel).

Potassium Benzoylpicraminate.—$C_6H_2(NO_2)_2$, $NHCOC_6H_5$ (ortho), OK, $2H_2O$.[1] Small beautiful reddish-yellow needles, which dissolve easily in water and dilute alcohol. Water-free, very dark red (Stünkel).

Barium Benzoylpicraminate. $(C_6H_2(NO_2)_2, NHCOC_6H_5, O)_2$ Ba. $5H_2O$.[1] Shellac-red needles. Dissolves in water with extreme difficulty (Stünkel).

Benzoylparamidodinitrophenol, or Benzoylisopicraminic Acid. C_6H_2OH, $(NO_2)_2NHCOC_6H_5$ (para). Reddish plates, having a splendid golden lustre. Quite soluble in alcohol and acetic acid, very little soluble in benzol and water. Melting point 250° C. decomposing.

Potassium Benzoylisopicraminate.—$C_6H_2(NO_2)_2NHCOC_6H_3$ (para) OK, H_2O. Fine red needles with a splendid golden lustre. Very easily soluble in water, somewhat less in alcohol. Water-free, brick-red.

Barium Benzoylisopicraminate.—$(C_6H_2(NO_2)_2$, $NHCOC_6H_5$, $O)_2$ Ba. $3H_2O$. Fine delicate red needles with a golden lustre. Dissolves in warm water easily; in cold, less easily. Water-free, dark red.

The larger part of this work was done in the chemical laboratory of the University of Göttingen, during 1879 and 1880, and I am indebted to Prof. H. Hübner for invaluable advice in connection with the investigations. I purpose further perfecting the determinations here reported, and pursuing the several lines of investigation which have been started, as rapidly as the spare time can be ound.

Laboratory of the N. C. Agricultural Experiment Station, Raleigh, *Dec.* 1882.

[1] Stünkel, Dissertat. Göttingen, 1880, 18.

PISCIDIA, THE ACTIVE PRINCIPLE OF JAMAICA DOGWOOD (*Piscidia Erythrina*).

By Edward Hart.

The fluid extract of Jamaica Dogwood, obtained from the bark of the root, has been introduced to the notice of the medical profession by Parke, Davis & Co., of Detroit, Mich., to whose kindness I owe a supply of material for this investigation. It is "stated by medical men to be a direct sedative, producing narcotic effects which are refreshing, and not followed, like opium, by hyperaemia of the brain, nausea and general nervous disturbance. It is said to be of value in bronchitis, asthma, nervous cough, writer's cramp, spasms of muscles due to functional causes, chorea, tetanus, and especially in toothache to relieve pain."[1] The physiological action of the extract[1] and also of the active principle[2] has been studied by Dr. Isaac Ott, of Easton. After many fruitless trials I succeeded in separating the active principle as follows: The contents of a pound bottle were poured into a flask in which 30 grams of quicklime had been slacked with enough water to form a thick paste. The lime was intimately mixed with the extract by shaking, allowed to stand in a warm place for half an hour, filtered and the residue pressed. Water was then added until the solution became slightly turbid. After standing two or three days, crystals of piscidia separate on the sides and bottom of the flask, accompanied with more or less resinous substance, from which they can be easily separated by recrystallization from alcohol. By adding water to the liquid poured off from the crystals of impure piscidia, a second crop of the crystals still more impure can be separated. I have succeeded in obtaining about ½ gram piscidia from each bottle of extract, which corresponds to 1 pound of the root bark. The resinous substance which separates on adding a large quantity of water to the filtrate from the piscidia crystals still contains piscidia in small quantity, but I doubt whether the total amount contained in each bottle can be much over a gram.

Piscidia, $C_{29}H_{34}O_8$.

The active principle after many recrystallizations from alcohol is obtained in the form of small, nearly colorless crystals, which appear under the microscope to consist of four or six-sided prisms.

[1] Ott. Detroit Lancet, June, 1880.

[2] Archives of Medicine, Feb. 1881.

It melts at 192° (uncorrected). Piscidia is insoluble in water, slightly soluble in cold, much more in boiling alcohol, only slightly soluble in ether, easily soluble in benzene and chloroform. It dissolves in strong hydrochloric acid, and is reprecipitated, apparently unchanged, by dilution with water. It dissolves in cold concentrated sulphuric acid and separates again by addition of water, but this treatment appears to change its properties, as it no longer dissolves easily in alcohol. Boiling with dilute and strong acid causes no separation of sugar. An alcoholic solution of lead acetate gives no precipitate. The alcoholic solution is neutral to litmus paper. The analysis resulted as follows:

(1) .1780 gram gave .4555 gram CO_2 and .0939 H_2O = 69.78 per cent. C and 5.86 per cent. H.

(2) .2323 gram gave .5942 gram CO_2 and .1077 H_2O = 69.76 per cent. C and 5.15 per cent. H.

(3) .1473 gram gave .3765 gram CO_2 and .0714 H_2O = 69.69 per cent. C and 5.38 per cent. H.

These combustions were made in a stream of oxygen. On examination the oxygen used was found to contain hydrogen,[1] no doubt derived from having been kept in a metallic (galvanized iron) gas-holder. It is well known that oxygen made from potassium chlorate contains a small quantity of chlorine. Another combustion was then made, the oxygen being passed through a red hot platinum tube before entering the apparatus used in drying the gas and freeing it from CO_2. Only the water was determined.

(4) .3660 gram gave .1642 gram HO_2 = 4.98 per cent. H.

	Calculated.		Found.			
			(1)	(2)	(3)	(4)
C_{29}	348	69.60	69.78	69.76	69.69	
H_{24}	24	4.80	...	...	...	4.98
O_8	128	25.60				
	500	100.00				

As far as could be ascertained the fluid extract owes its poisonous properties entirely to the piscidia it contains, at least the filtrate from the lime contains apparently no other substance except the resinous substance already mentioned. This appears to contain a little piscidia which cannot be entirely separated from it. I have not examined the lime precipitate.

LAFAYETTE COLLEGE, *Feb.* 1883.

[1] Compare Lieben, Annalen der Chem. **187**, 142.

Communications from the Chemical Laboratory of Rutgers College.

IX.—ESTIMATION OF CHLORINE, SULPHURIC ACID, AND CHROMIUM IN THE PRESENCE OF ORGANIC MATTER.[1]

By Charles T. Pomeroy.

The determination of chlorine, sulphuric acid, and chromium in the presence of organic matter, as in the case of the analysis of many dye-stuffs, is a matter of considerable difficulty. It is necessary to get rid of the organic matter by ignition with alkali carbonate and nitrate, else the determination of the chromium will not be reliable. During the oxidation of the organic matter a portion of the nitrate is reduced to nitrite, and on acidifying the solution, preparatory to the precipitation of the chlorine, the nitrous acid reduces some of the chromate to green chromous chloride, in the presence of which silver nitrate fails to precipitate the whole of the chlorine.[2] If an attempt is made to precipitate the sulphuric acid in this solution, it will be found that the barium sulphate retains chromic oxide.[3]

It becomes necessary, therefore, after destruction of the organic matter, to entirely convert the chromium into a chromic salt before the chlorine and sulphuric acid can be determined with accuracy. The reduction with alcohol is not practical in this case, since chlorhydric acid must be added. Neither can the reduction by means of hydrogen sulphide be taken advantage of; for, on standing in a warm place, there is danger, not only of losing chlorhydric acid, but also of oxidizing a portion of the hydrogen sulphide to sulphuric acid. The reduction with sulphurous acid is out of the question, for similar reasons.

The following method I have found to give satisfaction. To the solution of chromate containing sulphates, chlorides, chromates and salts of chromium, obtained by extraction of the mass which has been fused with alkali carbonate and nitrate, and filtration from the residue, which contains the iron, lime and magnesia, a solution of potassium, sodium, or ammonium nitrate is added and then

[1] This research was begun in the College Laboratory and finished in Mr. Pomeroy's private laboratory in Newark.—P. T. Austen.

[2] Peligot. Fres. Quant. Anal., Last Am. Ed. 432.

[3] Fres. Quant. Anal. 1876, 354.

nitric acid in excess. After standing in the cold for about twelve hours, ammonium hydroxide is added and the whole boiled, the precipitate of chromic hydroxide filtered off, washed with hot water (best with the aid of a filter pump) and estimated as usual. In the filtrate from the chromic hydroxide, the sulphuric acid is estimated as barium sulphate, by precipitation with barium nitrate and nitric acid. It is occasionally necessary to purify the barium sulphate by fusion with sodium carbonate and reprecipitation.

In the filtrate from the barium sulphate, the chlorine is precipitated by silver nitrate as usual.

In the presence of an alkali nitrite and nitric acid, the reduction of the chromic acid takes place immediately on boiling the solution. Advantage may be taken of this when it is required to determine the sulphuric acid alone, since in this case there is no danger of loss on boiling.

The chromates are reduced to chromic salts by the nitrite, which passes into nitrate, while the chromous salts are oxidized by the nitric acid into the chromic state.

The following analyses were made to test the accuracy of the method:

10 cc. of a dilute chlorhydric acid gave

	I.	II.	Mean.
AgCl	1.0794	1.0790	1.0792

Dissolved 2.4 grams or $K_2Cr_2O_7$ in 200 cc. water:

	I.	II.	III.[1]	Mean.	Calc.
25 cc. $K_2Cr_2O_7$ solution	.3000 gram	.3000 gram	.3000 gram	.3000 gram	...
	5 cc. HCl	5 cc. HCl	5 cc. HCl	5 cc. HCl	...
Cr_2O_3 found	.1561	.1559	.1550	.15566	.15543
AgCl "	.5397	.5399	.5391	.53956	.5396

In these analyses the acid was neutralized with ammonium hydroxide, sodium nitrite and then nitric acid added. It was not thought necessary to check the sulphuric acid determinations, as there was nothing in the method to interfere with this determination. In practice, the duplicate results agreed excellently.

In the analysis of commercial chrome-yellow by this method, the lead, even when present as sulphate and chloride, passes entirely into solution upon adding sodium nitrite and nitric acid in sufficient quantities and boiling.

[1] Nos. 1 and 2 were precipitated in glass, No. 3 in porcelain.

Sodium nitrite suitable for this purpose can be prepared by simply heating to redness for some time in a closed iron vessel, sodium nitrate, free from sulphates, chlorides, and silica, until nearly one molecule of oxygen has been driven off, and then dissolving the mass in water and filtering off the oxide of iron and other insoluble impurities.

The crude sodium nitrate can be purified by dissolving the commercial article in water, filtering, precipitating sulphuric acid, if it contains any, with barium nitrate, filtering, precipitating the barium with sodium carbonate, filtering, adding an excess of nitric acid, and heating with small additions of nitric acid, until free from chlorine, nearly neutralizing with sodium carbonate and then crystallizing.

The method of preparing sodium nitrite mentioned by Fresenius[1] has not proved satisfactory in my hands, as the one just given. In almost all cases the bottom of the iron vessel melts out. In one case, the iron bottom, which was a quarter of an inch thick, melted out within fifteen minutes at a hardly visible red heat. The product thus obtained is also very liable to contain but little nitrite, being almost all transformed into the hydroxide, and hence has but little reducing effect on the chromates. It is perhaps possible that the oxide of lead acts as a carrier of oxygen to the iron, taking up oxygen from the nitrate and giving it up to the iron. In this way a small quantity of lead oxide might effect the destruction of a large amount of iron.

NEW BRUNSWICK, N. J.

Contributions from the Chemical Laboratory of Harvard College.

XXX.—A MODIFICATION OF NOACK'S METHOD FOR PREPARING CARBONIC OXIDE.

BY LEONARD P. KINNICUTT.

In the Berlin Berichte, volume 16, page 75, E. Noack shows that carbonic oxide can be obtained by passing carbon dioxide over zinc dust. The idea that the same gas might be more conveniently made by heating carbonates directly with zinc dust, led me to try a series of experiments with magnesite. I found that

[1] Qual. Anal., Last. Am. Ed. 71.

when powdered magnesite mixed with twice its weight of zinc dust, is placed in a copper retort and heated so that the bottom of the retort is nearly surrounded by the flame, a gas is immediately given off, which, after the first five minutes, is nearly pure carbonic oxide. For the first five minutes, the gas is a mixture of carbonic oxide, carbon dioxide, and in case the substances were not perfectly dry, a little hydrogen. In place of a retort, hard combustion tubing can be used.

An analysis of the gas, when given off at the rate of about four bubbles a second, collected directly from the retort and measured over mercury, gave the following result:

Volume of gas 152.5. $P = 583.4$. $t = 4°$. Cor. $V = 115.4$.

After absorption of CO_2 by KOH: Volume of gas 150.0. $P = 588.8$. $t = 5°$. Cor. $V = 114.7$.

Per cent. $CO_2 = 00.61$.

I have undertaken the study of the decomposition of other carbonates, but as a method for preparing carbonic oxide the above is in every way satisfactory; the manner in which the gas is given off resembling that of oxygen when made from potassium chlorate, with the advantage that the evolution is more easily controlled.

March 17, 1883.

METHODS OF ANALYSING SAMARSKITE

AND THE OTHER COLUMBATES CONTAINING EARTHY OXIDES, BY THE AGENCY OF FLUORHYDRIC ACID; AND OF DISSOLVING COLUMBITE AND TANTALITE BY THE SAME ACID.—ON THE SEPARATION OF THORIA FROM THE OTHER OXIDES.—QUANTITATIVE ESTIMATION OF DIDYMIUM OXIDE IN ITS MIXTURES WITH OTHER EARTHY OXIDES.

BY J. LAWRENCE SMITH, *Louisville, Ky.*

The study of this class of minerals has always presented considerable interest to the analytical chemist, from the time of the discovery of columbite by Hatchett in 1801, and tantalite and yttrotantalite by Ekeberg about one year later. These minerals for more than twenty years were the only known columbites and tantalites; since then about fourteen other well-defined species have

been discovered and described, although the chemical formulæ of most of them are yet in doubt.

The metallic acids in these minerals have many interesting characteristics, which have already attracted special attention since H. Rose's researches in 1846 defining the distinctive characteristics of columbic and tantalic acid, which, prior to that date, had been considered by most chemists as being one and the same acid. M. Hermann, and later, M. Marignac, took up M. Rose's investigations and gave to them considerable extension. The former thinks that he has discovered two additional metallic acids of the same type in the minerals in which the first two are found. The metals of these acids he has called ilminium and neptunium.[1] The labors of M. Marignac, as set forth in his various publications,[2] have contributed very largely to our precise knowledge of certain very important compounds of these acids, and he has also given the only reliable method of a close quantitative separation of columbic and tantalic acid.

An interesting chemical characteristic of these minerals is, that nearly all of them have, as a portion of their bases, some one or more of the rarer earths, as the oxides of yttrium, erbium, cerium, thorium; and some new earths not yet fully defined. One reason for the comparatively imperfect study of the compounds of tantalum and columbium is the rarity of the minerals containing them; but since the discovery of comparatively large quantities of columbite and samarskite in the United States, this difficulty is removed. Another obstacle to their study arises from the method of decomposing them, this being attended with more or less inconvenience when large quantities are to be operated on. This last difficulty will, however, be removed to a considerable extent by the analytical facts to be detailed in this communication.

In my published investigations in connection with the columbic and tantalic acid minerals from new localities in the United States[3] (more especially the remarkable developments of samarskite in North Carolina), the object in view was to detail all that was connected with their mineralogy, to describe the new species I had discovered, and to give a clear idea of their constitution in com-

[1] Jour. für prakt. Chem. **15**, 105 Chemists are not ready to recognize these as new substances, but rather as mixtures of tantalic and columbic acids.

[2] Annales de Chim. et de Phys. **8**, 1866, 115-75.

[3] American Journal of Science, May, 1877, 360.

parison with the same minerals as found elsewhere. In the analyses in that paper I did not give the relative proportions of columbic and tantalic acids, assigning as my reason at the time for this omission that the method I had worked with (Rose's) proved too unsatisfactory to warrant the waste of time in seeking after results that I was satisfied would be inaccurate. In this view I was sustained by M. Marignac, who has devised a much better method, which I have since tried, and which gives very good approximate results, within 1½ to 3 per cent., according to the amount of tantalic acid present. In the same paper I stated that the earths in samarskite did not appear to contain cerium oxide as does the Ural variety of the same mineral, although in the analyses then given I preferred noting the earths of that group as cerium oxides[1] until I could arrive at more satisfactory conclusions by renewed researches; for it is known that a small quantity of cerium oxide mixed with other oxides of that group may escape detection when the entire amount of oxides treated is very small; so it was thought better to repeat the experiments on larger quantities before making any conclusive statement as to the presence or absence of cerium oxide. Thoria, also, if present in the North Carolina samarskite, was there in too minute a quantity to warrant me in pronouncing upon it by the usual method of separation. All doubt, however, on this head has been dispelled by an easy and certain method I have discovered of separating it from the other earths, and, although present in the proportion of less than 1 per cent. of the mineral, it can be separated and identified as well as any other constituent of the mineral, and that by operating with not more than three or four grams of the mineral.

Method of Decomposing and Analysing Samarskite.

I shall first detail the method pursued in the analyses of samarskite, as this being one of the most complex of the columbates, all that is said in regard to it will be applicable to other forms of this class of natural compounds. The method most commonly employed for decomposing this mineral is by means of potassium bisulphate in the proportion of one part of mineral to six of potassium salt. This, it will be seen, introduces a very large amount of solid matter into

[1] By this group is meant all the oxides forming insoluble double salts with the potash and soda sulphates, amounting to about 4 per cent. of the mineral. Thoria, if present, was to be sought for among the oxides.

the process, and besides, requires careful heating to redness for some time. A more recent and better method is that proposed by Prof. Wolcott Gibbs,[1] viz. by the acid potassium fluoride (FlKFlHO). This method was used by M. Marignac in his most admirable and exhaustive labors on tantalic and columbic acid compounds already referred to. Concentrated sulphuric acid when heated with some of the columbates will decompose them more or less, but cannot be used in their analysis. The method about to be described is a decided improvement on either of the above, for reasons that will be rendered very apparent.

Decomposition by Fluorhydric Acid.[2]

The quantity of samarskite used in the analyses is usually five grams, and having an abundance of the material, special portions are used for the verification of certain results. The precipitates of all of the ingredients are so dense and granular that filters 7 to 10 cm. in diameter are used except in the iron precipitate. The mineral is triturated to a fine powder, and five grams, dried at 150° C.,[3] weighed and placed in a small platinum capsule; one of 50 cc. capacity is sufficiently large. This is moistened with about 5 or 6 cc. of water, and then from 8 to 10 cc. of concentrated fluorhydric acid is added (one-half at a time with an interval of two or three minutes), and the mixture stirred with a platinum rod. In a few seconds a vigorous action takes place; the mass becomes heated, and in from five to ten minutes the decomposition is complete without the application of heat. If the powder be exceedingly fine the decomposition is almost as rapid as that of calc-spar when chlorhydric acid is poured upon it.

The action is known to be complete by the disappearance of every black particle in the mass. The capsule is now placed on the

[1] American Journal of Science, **37**, 355.

[2] Not many years ago this acid was made and used in comparatively small quantities, but owing to the extended use of it in the arts, it is now manufactured on a large scale. One of the largest manufacturers of this acid in this country is Feuchwanger, 118 Dey Street, New York, who furnishes a *fuming acid*, remarkably pure for a commercial article, at 25 cents per pound, in lead jugs of 30 lbs. capacity. The saturating property of 10 grams of this acid is equal to that of 23 grams of nitric acid of 1.42, costing 12 to 14 cents by the carboy, making the fluorhydric acid actually cheaper than the nitric acid. I have found in many laboratories what purports to be fluorhydric acid that is little less than sour water. When I desire pure fluorhydric acid, I distil the commercial acid of Feuchwanger in a small platinum still and condense in a very little distilled water, the vessel being surrounded by ice. In this way there is no annoyance from fluorsilicic acid.

[3] Avoid heating to redness, for by so doing the mineral is not so readily acted on by the fluorhydric acid. I determine the loss by heat on a separate portion of one gram.

water-bath to ensure complete decomposition and to evaporate away the larger portion of the liquid.

After the reaction the contents of the capsule are, 1st, a clear colorless solution; and 2d, a heavy green precipitate. The *solution* contains all the metallic acids, oxides of iron and manganese. The *insoluble portion* contains all the earths and uranium oxide. It is true that traces of iron will be subsequently found in the analysis of the insoluble part and traces of earth in the solution, but they are easily separated in the course of the analysis and properly placed in the estimates. They, however, only represent a fraction of one per cent.

It will be seen that thus far in a very few minutes the samarskite has not only been decomposed but partly analyzed, for this perfect separation into two parts facilitates to a vast extent the subsequent operations.

To the contents of the capsule, decomposed as above stated, 30 cc. of water are added, the whole is then warmed and thrown on a filter (8 cm.) in a gutta-percha or silver funnel, the filtrate being received in a platinum capsule. The filtration takes place very rapidly and the precipitate is well washed with hot water, a few drops of fluorhydric acid being added towards the end of the washing, to prevent a trace of the precipitate passing through the filter, which might otherwise occur. The filtering and washing is accomplished in fifteen or twenty minutes. As already stated we have two classes of substances completely separated from each other, one soluble, the other insoluble. The soluble we call A, the insoluble we call B.

We will first consider A. This solution is evaporated over a water-bath, and before it reaches dryness, concentrated sulphuric acid is added in excess to decompose the fluorides, about 1 cc. acid to every gram of metallic acid supposed to be present. The evaporation is completed by careful heating over the flame until the decomposition is complete and nearly all the sulphuric acid has been driven off. After cooling, water is added acidulated with chlorhydric acid, the contents of the capsule washed out into a glass flask capable of holding one litre. When 5 grams of the mineral have been used the liquid mass should be half a litre. A little chlorhydric acid is added. This is now boiled for one or two hours,[1] which can be done in an ordinary bottle.

[1] In my laboratory the boiling of liquids containing a heavy precipitate is always accomplished by driving steam through from a glass flask or small boiler, with two tubes, one bent at two right angles to drop in the liquid, and the other a straight one for a safety tube, thus preventing all thumping.

After boiling, the contents of the vessel are thrown on a filter and thoroughly washed with hot water. The insoluble part remaining in the filter is columbic and tantalic acids with a little tungstic and stannic acid. This is dried, ignited and weighed with all the usual precautions, and afterwards the tungstic and stannic acids are separated in the manner described by Rose, and the columbic and tantalic acids by Marignac's method.[1]

The filtrate from the metallic acids is concentrated, and as it contains only iron and manganese, with mere traces of other oxides, they are separated and estimated in the usual way by the sodium acetate method. This disposes of part A.

We now pass to the portion B, which is the insoluble part remaining after the first treatment with fluorhydric acid, and is composed of the fluorides of the earths and uranium. It is washed from the filter into a small platinum capsule. To this sufficient concentrated sulphuric acid is added to decompose the fluorides (about 2½ grams suffice where 5 grams of minerals are used), and the whole is concentrated as far as possible over a water-bath, and carefully heated over the flame until the excess of sulphuric acid is driven off, or very nearly so. After cooling, about 50 cc. of water are added and the capsule is gently heated on a water-bath, when the mass dissolves completely, furnishing a bright green solution. A minute amount of insoluble matter may sometimes show itself; this belongs to the metallic acid, and is separated and added to that obtained from A. It is usually only a few milligrams. The green solution is heated over the flame and a little nitric acid is added, when the color is changed to a lemon yellow, from the higher oxidation of the uranium oxide. The solution is now introduced into a beaker and increased to about 250 cc. by the addition of water, and made to boil. It is then very nearly neutralized by ammonia, and oxalic acid or ammonium oxalate added very gradually. The precipitate, as is well known, will be first taken up and afterward become permanent. It consists of all the earths present. This is allowed to stand some 6 or 8 hours, then thrown on a filter and well washed. This oxalate of the earths I will call C, and proceed to treat of it a little further on. The filtrate contains all the uranium in solution with a trace of iron. This is concentrated to about 80 or 100 cc., and then a concentrated solution of ammonium carbonate is added, which first precipitates the

[1] Annales de Chim. et Physique, 8, 1866, 115–175.

uranium oxide and then redissolves it. The solution is nearly clear with the exception of a few flocci of ferric oxide. This is warmed gently and a few drops of ammonium sulphide are added, which precipitates every trace of iron. That is washed and estimated in the usual way, and represents from two- to three-tenths of one per cent. of the mineral, and is added to the ferric oxide obtained from solution A. The filtrate containing the uranium oxide is evaporated to dryness, the ammonium salts driven off, and the oxide estimated by the ordinary method. In all the analyses thus far no solid matter is introduced by the reagents.

Before quitting this part of the subject I would state that there is no columbate that does not readily yield to this treatment by fluorhydric acid, as euximite, hatchettolite, fergusonite, etc., and so completely separate these minerals into two classes of substances (the metallic acids in a state of solution and the earths as insoluble compounds) that the weighing of the acid decomposed by the action of sulphuric acid as described will give at once an idea of the quantitative composition of the minerals.

Columbite and Tantalite.

It is well to make some remarks in reference to the columbite and tantalite and their decomposition by fluorhydric acid, for they are more difficult to decompose by any method than are the columbites of the earths.

Before we had the more powerful and convenient methods of decomposing minerals, Berzelius, Rose and others had to resort to the finest possible subdivision of the mineral, often using a flat slab of agate and triturating with water. This fine trituration is sometimes, even now, employed in our present modes of manipulation. As the method I have adopted for years is more convenient than any I know of in use, it will not be out of place to refer to it here, for the whole operation is conducted in the same mortar in which the crushed mineral is first powdered.

If we have columbite to decompose, exceedingly fine dry trituration in an agate mortar suffices. To triturate properly, one gram of columbite will require from ten to fifteen minutes in a four-inch mortar. Thus pulverized, place the mineral in a platinum crucible or capsule, and add about five grams of fluorhydric acid of the strength alluded to in the first part of the paper; then heat over the flame on a plate of iron, so as to bring the temperature up to

from 60 to 90 C. A half an hour suffices for complete solution; if any black powder remains, it is well to add a little more acid and heat again. A few flocci will sometimes appear in the solution, which is stannic oxide. In the analysis of tantalite the solution is not so easily accomplished, but I overcome that completely by my modification of the trituration of the mineral. After rubbing it up in the mortar for about five or six minutes I add a little strong commercial (95 per cent.) or absolute alcohol to the contents of the mortar, enough to cover completely the powder, then continue the trituration. The alcohol will soon evaporate; add a fresh portion; this I may have to repeat several times. The alcohol, like any other liquid, enables the pestle to reach thoroughly the coarser particles that always settle to the bottom. To triturate thoroughly, one gram of the tantalite requires about twenty minutes. The contents of the mortar are like imperfectly dried mud, and are kept at a temperature of about 150° C. in an air-bath for ten or fifteen minutes. A gram of the material is then placed in a capsule or crucible of platinum, thoroughly dried and carefully weighed. About five grams of the fluorhydric acid are now added, and the heating conducted as in the case of columbite. A half-hour suffices to complete the solution, which is a clear liquid with a few white flocci in it that I have proved to be stannic oxide. While this method of solution appears to be a little tedious, I can assure those who try it, that the manipulations are very simple, and there is no soluble matter introduced, as is the case when six or eight times its weight of potassium bisulphate is used. We now evaporate the solution of either columbite or tantalite to dryness, proceed as in the case of the samarskite. As there are no earths, however, in these minerals, there is little else than iron and manganese to deal with as associated with the metallic acids, which are decomposed by sulphuric for separation from iron and manganese as already indicated.

In regard to the separation of the two acids when they are in the same mineral, I use the method already referred to and first used by Marignac.[1]

The tungstic acid, stannic acid, etc., I estimate in the manner pointed out by Rose in his Analytical Chemistry.

(*To be continued.*)

[1] Annales de Chimie et de Physique, **8**, 60; 1866.

REVIEWS AND REPORTS.

On the Present Condition of the Soda Industry.[1]

From information kindly supplied to me by manufacturers in all the countries in which the soda industry is practised, I have been enabled to draw up a statement of the present total soda production of the world, and of the proportions in which that production is divided between the Leblanc process and the ammonia process. In drawing up the following table I have converted all the figures supplied to me, alike those for soda ash, those for crystals, those for caustic soda, those for bicarbonate, and those for black ash sold as such, into terms of pure Na_2CO_3:

Present Soda Production of the World.

	Leblanc Soda.	Ammonia Soda.	Totals.	Ammonia Soda per cent. of Total Soda.
Great Britain . .	380,000	52,000	432,000	12.0
France	70,000	57,125	127,125	44.9
Germany . . .	56,500	44,000	100,500	43.8
Austria	39,000	1,000	40,000	2.5
Belgium . . .	...	8,000	8,000	100.0
United States . .	...	1,100	1,100	100.0
Total . .	545,500	163,225	708,725	23.0

This table shows that the total quantity of soda now being manufactured annually is nearly 710,000 tons, and that of this quantity more than 163,000 tons are produced by the ammonia process.

Although it is now more than 47 years since the ammonia process was first proposed by Dyer and Hemming, it is less than 17 years since that process was first realized industrially. As an industrial process, capable of being worked continuously and with satisfactory commercial results, the ammonia process dates only from 1866, being the year in which M. Ernest Solvay, of Brussels, began to produce ammonia soda at works which he had established for the purpose at Couillet, near Charleroi. M. Solvay has now two other ammonia soda works in operation—one in France, at Varangeville-Dombasle, near Nancy, and one in South Germany, at Wyhlen, in the Grand Duchy of Baden—and by his courtesy I am enabled to place before you the following statement of the quantities of ammonia soda which he has manufactured in each complete twelve months from the first of May, 1866:

[1] Abstract of a paper read by Walter Weldon before the Society of Chemical Industry, and published in the Journal of the Society.

	Tons.	
1866-67	179	Couillet only.
1867-68	465	
1868-69	719	
1869-70	940	
1870-71	1,862	
1871-72	2,805	
1872-73	3,423	
1873-74	3,980	
1874-75	4,678	
1875-76	5,768	Couillet and Dombasle.
1876-77	11,579	
1877-78	19,247	
1878-79	25,023	
1879-80	32,326	
1880-81	42,669	Couillet, Dombasle, and Wyhlen.
1881-82	53,400	

The competition of the ammonia process with the Leblanc process has thus attained its present degree of seriousness only very recently indeed.

While face to face with so serious an amount of competition, actual and imminent, on the part of the ammonia process, the Leblanc process pure and simple is now further threatened with what is surely the "most unkindest cut of all," namely, with competition from the Leblanc process itself—combined with the extraction of copper from Spanish pyrites.

To explain how this has come about I must remind you that the sulphuric acid used in the Leblanc process is now invariably manufactured from the sulphur of pyrites; that the pyrites used in this country is now almost exclusively either Spanish or Portuguese pyrites, containing two or three per cent. of copper and very small quantities of silver and gold; that after most of the sulphur has been burnt off from the pyrites, as the first step in the manufacture of sulphuric acid, the residual "burnt ore," or "pyrites cinders," as it is called, is treated by the wet way for the extraction from it of copper, and in most cases now of gold and silver also;[1] and that what remains when these have been extracted is an almost pure oxide of iron, which finds a ready sale for use for various purposes in connection with the manufacture of iron and steel. The supply of this cupreous pyrites is for the most part monopolized by three great companies—the Tharsis Company, the Rio Tinto Company, and Messrs. Mason and Barry. These companies not only supply

[1] A German analysis of Rio Tinto pyrites gives the following results per 1000 kilos:
495 kilos. Sulphur.
430 kilos. Iron.
30 kilos. Copper.
10 kilos. Lead.
26 grams Silver.
180 milligrams Gold.
150 grams Bismuth.

nearly the whole of the pyrites used in the manufacture of sulphuric acid in England, but the Rio Tinto Company also supplies annually some 60,000 tons of pyrites to Germany, and is also beginning to send pyrites into Austria. None of the three companies, however, has been able to sell an ounce of pyrites in France.

The course, then, which the Rio Tinto Company is taking is this. Unable to sell its pyrites to the French Leblanc soda-makers, it has determined that the Leblanc soda made in France, or at least a large part of it, shall nevertheless be made by means of Rio Tinto pyrites, and to this end it has promoted a subsidiary company, "La Compagnie d'Exploitation des Minerais de Rio Tinto," which company is to make Leblanc soda in France and elsewhere, relying for its profits neither on soda nor on chlorine, but on copper and oxide of iron. For this company soda and chlorine will be simply by-products, which it will be glad to sell at a profit, if that may be, but which, if that may not be, it will be content to sell at the bare cost of manufacturing them. It will manufacture them only for the sake of converting Rio Tinto pyrites into pyrites cinders.

This new company proposes to operate upon an enormous scale. It has a capital of £1,200,000 sterling, of which one-half is already paid up, and there is talk of its building in France no fewer than five great works: one of which, designed and to be managed by Englishmen, it has already commenced, in the neighborhood of Marseilles. The result cannot but be grave for the existing French Leblanc soda-makers, and must inevitably affect the makers, both of Leblanc soda and of ammonia soda, in this country also.

Moreover, this new company will not confine its operations to France. Not only will it take Spanish pyrites to the United States and there make sulphuric acid, extract copper, and obtain "purple ore,"—large quantities of which at present go from England to America,—but it will also build a large soda-making and copper-extracting works—which will certainly affect the English alkali trade—in the neighborhood of Antwerp. The Leblanc process will thus be reintroduced into Belgium, not as a substantive process, but simply as a part of a combination of processes for the utilization of cupreous pyrites.

To such complexion has the Leblanc process come at last. Originally, soda was its only commercial product, the hydrochloric acid produced during the first stage of it being turned to no account. In time, a demand grew up for chlorine, that hydrochloric acid began to be utilized, and the manufacturers of Leblanc soda now sent into the market two products, by each of which they gained profits. Then their soda ceased to be profitable, and became a kind of by-product, which they continued to make only because they could not otherwise make chlorine. Now, Leblanc soda gives no profit at all, and chlorine none to speak of; and both have come to be regarded as secondary products, to be made only incidentally, and only because making them is essential

to the application to certain ores of the wet method of extracting copper.

Returning to the ammonia process, when that process first began to threaten them, the makers of Leblanc soda comforted themselves by two considerations: one of which was that the ammonia process must itself tend to check its own extension, by reason of the loss of ammonia inseparable from that process so increasing the demand for ammonia as to materially raise the price of that body. They knew that the constantly increasing demand for ammonia for the purposes for which it was already employed had doubled its price within twenty years; and they thought that every further extension of the ammonia soda process must still further increase the market value of ammonia, until at length the ammonia process would cease to have any advantage over the Leblanc process. So far, however, from that anticipation having been realized, despite the immense extension which the ammonia-soda process has recently undergone, the price of ammonia is now beginning to fall. The delusion that it was impossible to collect the ammonia given off from coke ovens without spoiling the coke is at last giving way before accomplished facts. Ammonia is now being obtained commercially, not only from coke ovens, but also from another source, wholly unforeseen and unexpected; and the time, moreover, seems at last to have dawned when there will be collected and utilized as ammonia at least a portion of the nitrogen of nearly all the fuel burnt either for industrial or for domestic purposes. In France ammonia has been collected from coke ovens for a number of years past.

Mr. William Ferrie was struck by the idea that the methods employed for separating ammonia and tar from crude illuminating gas might be used for separating the same bodies from the gases from blast furnaces in which raw coal is used; and although the volume of the gases from such furnaces, per ton of coal employed, is about thirteen times greater than that of the gases obtained by distilling the same kind of coal in retorts—is not less, that is to say, than 130,000 cubic feet—Mr. Ferrie's idea has been put into execution with complete success. From two of the sixteen blast furnaces at the Gartsherrie Ironworks ammonia and tar have been regularly collected for some months past, and the preparations are in progress for collecting them from the other fourteen blast-furnaces there. The quantity of ammonia at present being obtained at Gartsherrie is the quantity corresponding to about 18 cwt. of ammonium sulphate per day, being at the rate of 20 lb. of ammonium sulphate per ton of coal consumed.

Each of the one hundred and twenty Scotch blast-furnaces consumes, on an average, fifty tons of coal per twenty-four hours. The total quantity of coal consumed in them per annum is thus $50 \times 120 \times 365 = 2,190,000$ tons. The quantity of ammonia yielded per ton of coal being, as I have said, the quantity corresponding to 20 lb. of ammonia sulphate, there can thus be obtained

per annum from these 120 blast-furnaces a quantity of ammonia corresponding to nearly 20,000 tons of ammonium sulphate, worth, at the present selling price of that commodity, not less than £400,000.

Large, however, as is this quantity, it is only one-tenth of the further quantity which can be obtained from English coke ovens. The quantity of coal coked annually in England is not far short of 20,000,000 tons, and if Mr. Jameson's system were applied to the whole of our coke ovens, with the result of collecting, per ton of coal treated, the same quantity of ammonia as is obtained from the Gartsherrie blast-furnaces, there would be obtained from this source per annum the quantity of ammonia corresponding to 180,000 tons of ammonium sulphate, at present worth more than three and a half millions sterling. Nor is even this all; for I shall have to speak in a moment of another possible, and I believe probable, source of ammonia, even more extensive still.

Now, of the ammonia employed by the ammonia soda-maker, he loses from one-fiftieth to one-fortieth part. As he has to employ from one and a half to one and three-quarter equivalents of ammonia for each equivalent of sodium carbonate finally obtained, we may take it that he loses about one twenty-third of an equivalent of ammonia for each equivalent of sodium carbonate manufactured. In terms of ammonium sulphate, being the terms in which the loss of ammonia in the ammonia-soda process is usually stated, this loss corresponds to about five and a half parts of ammonium sulphate per hundred parts of sodium carbonate produced. The total annual loss of ammonia in the manufacture of the 163,000 tons of ammonia soda now being produced per annum thus corresponds to just about 9000 tons of ammonium sulphate. This is no doubt a large quantity of a commodity worth £20 per ton; but, in comparison with the extent of the new sources of ammonia which have just begun to be turned to account, it is utterly insignificant. It is less than one-twentieth part of the quantity capable of being yielded by blast-furnaces and coke ovens in Great Britain alone, and is a smaller fraction still of the quantity which, I believe, can be obtained from another source which has yet to be mentioned. We may therefore be quite certain that the progress of the ammonia soda process will not be hindered or limited by any difficulty as regards supply of ammonia.

The other consideration to which I referred as having given comfort to the makers of Leblanc soda, and which constituted indeed their chief ground of hope for salvation against the ammonia process, was that the world requires chlorine as well as soda, and that while the chlorine of the salt decomposed by the Leblanc process is yielded as hydrochloric acid, from which free chlorine can be obtained readily, the chlorine of the salt decomposed by the ammonia process is yielded as a somewhat dilute solution of calcium chloride. It was thought that the ammonia process would eventually even help the existing Leblanc soda-makers, by

preventing the further extension of the Leblanc process, and so restricting the production of hydrochloric acid, and thereby at length increasing the value of that body. The ammonia process, no doubt, would have produced that result, and would have produced it by this time, if the supply of hydrochloric acid in this country had not been already so largely in excess of the demand for chlorine products. That demand is always becoming larger, and within the last few years the production of hydrochloric acid has appreciably diminished; but in this country the constantly increasing stringency of legislative enactments with respect to river and air pollution has compelled so many producers of hydrochloric acid, who would have preferred to throw their acid away, to employ it in the manufacture of chlorine, whether that manufacture were profitable or not, that the selling price of chlorine products has of late years been continually falling, until it is now at a point at which it barely pays their cost. No doubt, if all the other conditions of the problem were to remain as at present, the demand for chlorine products would in time overtake the supply of hydrochloric acid in this country, as it has long since done on the Continent, and the manufacture of chlorine in England would so again become profitable. But the other conditions of the problem are not likely to remain stationary, and both M. Solvay and myself are doing our best to change them.

M. Solvay is proposing to manufacture hydrochloric acid from the residual calcium chloride of the ammonia process. I imagine that he is urged to that course, not merely by a desire to turn that calcium chloride to account, but also by a desire to avoid making too much nuisance. Neither calcium chloride nor sodium chloride will do much harm to a river, if sent into it in moderate quantities; but when it comes to sending into a comparatively small stream, far inland, 260 tons of calcium and sodium chlorides per twenty-four hours—say about ten tons per hour, night and day, all the year through, and M. Solvay must be doing something very like that at Dombasle—the matter assumes quite another aspect.

Be all that, however, as it may, M. Solvay is now erecting at Dombasle apparatus for an industrial trial of a process for obtaining hydrochloric acid from calcium chloride, at which he has been working for many years. The process in question consists in first concentrating by evaporation the mixed solution of calcium and sodium chlorides which is the residual product of the ammonia process; then mixing the concentrated solution with clay, making the mixture into balls, and drying these balls; and then heating these balls to redness in a current of steam. This process certainly works, on condition that the temperature employed be sufficiently high, and that the quantity of steam used be largely in excess of the quantity necessary to react upon the calcium chloride. As the resulting mixture of vapor and water and vapor of hydrochloric acid would otherwise give an extremely dilute aqueous acid, M. Solvay proposes to separate from it most of its vapor of water,

before condensing its hydrochloric acid, by passing the mixture of the two vapors through a very strong solution of $CaCl_2$, which he finds will absorb most of the steam from such a mixture, allowing the HCl to pass on alone, so that it can afterwards be condensed in the usual way. All this is ingenious, but it can hardly be cheap. First, a solution, containing only about eight per cent. of calcium chloride has to be evaporated, we might say to dryness; then the mixture of $CaCl_2$ and clay has to be maintained at a red heat for a considerable time in a current of steam; and then the solution of calcium chloride used to separate steam from the resulting mixture of steam and HCl has to be prepared for use again by having all the water which it has absorbed evaporated off from it. To English manufacturers who have more hydrochloric acid than they can use, this process of M. Solvay's will seem little less than ridiculous; but one must remember that it is intended for countries in which the demand for hydrochloric acid exceeds the supply, and in which countries, moreover, chlorine products are protected by import duties. In such countries one can quite conceive its being commercially practicable: in which case the exportation of chlorine products from England to the Continent is doomed. I ought to add that M. Solvay expects that the silico-aluminate of calcium, which remains after the chlorine of his mixture of calcium chloride and clay has been driven off by steam, will be useful as a cement, and will thus help to pay the cost of his hydrochloric acid.

The exportation of chlorine products from England to the Continent is, moreover, threatened in another way. The continental manufacturers of Leblanc soda, unlike the English manufacturers of Leblanc soda, do not produce enough hydrochloric acid to meet the demand of their respective countries for that acid itself and the products which are made from it. This is partly due to the production of ammonia soda, proportionately to the total production of soda, being so much greater in France and Germany than in this country, and partly to hydrochloric acid being required in those countries for industries which in this country do not exist. Large quantities of chlorine products consequently go to the Continent from this country: our production of hydrochloric acid being still sufficient to enable us to supply not only the total English demand for chlorine and the total American demand for chlorine, but also an appreciable proportion of the Continental demand for chlorine, and, in addition to all that, to throw a large residue of hydrochloric acid into the North Sea. The Continental Leblanc soda-makers do not like this importation into their respective countries of chlorine products from England; but they can prevent it only in one or other of two ways: either by increasing their production of hydrochloric acid, or by becoming enabled to obtain from a given quantity of hydrochloric acid a larger proportion of free chlorine than is yielded by the process at present in use. Personally, I have for the process at present in use that respect which one always feels for the bridge which has carried one

over, but I am well aware that it can by no means be regarded as final. It yields chlorine cheaply; but it yields only one-third of the total chlorine contained in the acid employed, the other two-thirds being lost as calcium chloride. English chlorine manufacturers will regard almost with horror the idea of a new chlorine process which shall yield in the free state practically the whole of the chlorine contained in the acid employed; but on the Continent there is a demand for such a process—a demand which will no doubt be lessened, but will by no means be destroyed, by what is being done in France by the Compagnie d'Exploitation—and I am one of those who have been called upon to endeavor to supply that demand. M. Pechiney is now preparing to make at Salindres a trial on an industrial scale of a process which, I think, will supply it; and by the end of this year he will probably have obtained decisive results.

As regards the English chlorine industry, however, I do not think that its prospects are by any means so gloomy as, from what I have said so far, might at first blush appear. But I think that its salvation will come from an unexpected quarter. I think that our English manufacturers of Leblanc soda will have to cease to devote their hydrochloric acid—when they do not throw it away—exclusively to chlorine making. They would, of course, be only too glad to do so, if a means could be furnished them of turning it to account otherwise. But the difficulty hitherto has been as to how to turn it to account otherwise. I believe that that difficulty is about to disappear. I am not free to enter into that matter now, and, indeed, it is not yet ripe for discussion; but I have very great confidence that new applications of hydrochloric acid, admitting of being applied very extensively, at comparatively small expense, are among the things of the immediate future.

There has come to me from Newcastle a very bold, but I venture to think, quite practical suggestion, the result of which can hardly fail to be of enormous importance, not only to the soda industry but to almost all industries whatever. That suggestion is that the soda-maker should entirely cease to use raw coal as fuel, but should convert all his coal into coke, collecting for sale the oil and ammonia evolved during its conversion into coke, and himself using for heating purposes the gases evolved during the coking operation and the coke itself. It is believed that, in the Newcastle district at any rate, by this mode of proceeding the soda-maker would obtain his fuel virtually for nothing. In that district there is produced per annum some two millions of tons of very small coal or "duff," which is almost a waste product, and which, singularly enough, yields more oil than the more costly kinds of Newcastle coal, while at the same time yielding a very fair coke, sufficiently good, at any rate, for use in the furnaces of chemical works, especially when its combustion is assisted by that of the gases from the ovens in which the coke is produced; and the value of the oil and ammonia obtained when this "duff" is coked in ovens to which

the Jameson system is applied is greater than the cost of the "duff" *plus* the cost of coking it. And it is probable that improved condensing arrangements will render the yield, if not of oil, at any rate of ammonia, so much greater than the yield hitherto actually realized, as to enable the same result to be obtained in the case of ordinary steam coal, not only in the Newcastle district but in the Lancashire district also. If so, the cost of producing Leblanc soda in both districts will be diminished by almost the total amount of the present cost of Leblanc soda for fuel. I say "almost," because, so far as one can see, the use of raw coal for "mixing" in the black ash process must still be continued.

And it seems to me that this idea cannot but be as applicable to almost all other industries as to the soda industry, while the result to the material well-being of mankind of its general application it is utterly beyond the power of any imagination adequately to conceive. This idea means, among other things, cheaper fuel for all purposes, an enormously increased supply of agricultural produce, and the entire suppression of smoke, even in the busiest centres of industry.

And for my own part I venture to think that the same idea might be applied even to the fuel required for domestic purposes, rendering London absolutely free from smoke, and pea-soup fogs things only of tradition. I think that the time will come when our gasworks will be replaced, at least to a large extent, by establishments in which coal will be treated for the production of coke, illuminating oils, ammonia, and heating gases; the coke to be burnt in our domestic fire-places, the oils to be used for lighting the interiors of our houses, the ammonia to be employed in agriculture, to cheapen and render more abundant our supplies of food, and the gases to be burnt for raising steam for driving dynamos for lighting our streets by the electric arc.

Recent Researches on the Pyridine and Quinoline Bases.

Ever since it was shown that a close connection exists between some of the important natural alkaloids and the derivatives of pyridine and quinoline, researches intended to aid in determining the nature and relationships of these derivatives have become more and more numerous, and at present the greatest activity prevails in this field of chemistry. All the evidence accumulated thus far is in harmony with the view that many of the important alkaloids are derivatives of pyridine, in the same sense that the so-called aromatic compounds are derivatives of benzene; and as the study of the isomeric derivatives of benzene has led to important synthetical results, so similar work in the pyridine series will probably lead to the synthesis of some of the alkaloids.

Pyridine Series, $C_nH_{2n-5}N$.—These bases were discovered by Anderson in bone oil, and found by Thenius to be present in coal tar. Cahours and Etard, in 1880, succeeded in obtaining them from nicotine by dry distillation. As thirty years had elapsed since the time of Anderson's work, and these bases had in the meantime assumed a considerable degree of importance, Richard and Weidel, and Herzig again undertook the study of bone oil. As a result of their labors we now know that, besides pyridine, there are present in bone oil two isomeric picolines, two lutidines and two collidines. Perkin, in 1865, first observed the artificial production of pyridine by the action of nascent hydrogen on azodinaphthyldiamine, and since then the synthesis of this base has been frequently attempted. Methods have been described by Chapman and Smith, by Ramsay, and more recently by Königs, which yield small quantities of pyridine, but for its preparation in quantity we are still dependent upon bone oil. To obtain pyridine and its homologues, bone oil is warmed with dilute sulphuric acid, the filtered solution precipitated with sodium hydroxide, and the free bases separated by fractional distillation.[1] The most rapid method of obtaining pure pyridine is to distil the calcium salt of nicotinic acid with lime.[2] Of the three picolines theoretically possible Weidel has found two in bone oil, while Baeyer[3] has made a third by the distillation of acrolein-ammonia. Lutidine had not been made synthetically until very recently. Hantzsch[4] describes a method which enabled him to make the first four members of this series of bases. By heating acetoacetic ester with aldehyde-ammonia in the proportion of two molecules of the former to one of the latter, there is formed a crystalline condensation-product which is the ester of dihydro-collidine-dicarbonic acid $(C_2H_5OOC)_2C_8H_{11}N.H_2$. By the oxidizing action of nitrous acid two atoms of hydrogen are removed, and there remains the ester of collidine-dicarbonic acid. This by saponification yields the corresponding acid, which when distilled with lime gives collidine,

$$\underset{\text{Collidine-dicarbonic acid.}}{C_5(CH_3)_3(COOH)_2N} - 2CO_2 = \underset{\text{Collidine.}}{C_5(CH_3)_3H_2N}.$$

By careful oxidation with potassium permanganate, collidine dicarbonic acid yields three successive oxidation products, each of which in turn can be converted into its corresponding base. Thus the first oxidation product gives lutidine,

$$\underset{\text{Lutidine-tricarbonic acid.}}{C_5(CH_3)_2(COOH)_3N} - 3CO_2 = \underset{\text{Lutidine.}}{C_5(CH_3)_2H_3N};$$

the second, picoline,

$$\underset{\text{Picoline-tetracarbonic acid.}}{C_5(CH_3)(COOH)_4N} - 4CO_2 = \underset{\text{Picoline.}}{C_5(CH_3)H_4N};$$

[1] Richard, Bulletin de la Société Chimique, **32**, 487.
[2] Laiblin, Annalen der Chemie, **196**, 159. [3] *Ibid.* **155**, 283. [4] *Ibid.* **215**, 1.

and the third, pyridine,

$$\underset{\text{Pyridine-pentacarbonic acid.}}{C_5(COOH)_5N} - 5CO_2 = \underset{\text{Pyridine.}}{C_5H_5N}.$$

Other methods for the preparation of collidine are known. Baeyer and Ador[1] have obtained it by heating an alcoholic solution of aldehyde-ammonia to 120°. Krämer,[2] by heating ethylidene chloride with alcoholic ammonia, observed its formation; while more recently Würtz[3] obtained it by the distillation of aldol-ammonia. The higher members of this series, parvoline, corridine, rubidine and viridine, have not yet been made synthetically.

The hypothesis of Körner, according to which the pyridine molecule is regarded as benzene in which one of the six CH groups is replaced by an atom of nitrogen, has found additional support during the last three years. Accepting this hypothesis, but one pyridine is theoretically possible, and indeed it has been found that from whatever source obtained, whether from bone oil, from coal tar or from nicotine, cinchonine or quinoline, pyridine always has the same boiling point, the same specific gravity and the same physical and chemical properties. Picoline, the second member of the series, being regarded as a methyl derivative of pyridine, three isomers are possible, and corresponding to each there should be a pyridine-monocarbonic acid. Three picolines are known, and Weidel and Herzig[4] obtained the third pyridine monocarbonic acid possible by heating lutidinic acid. Nine lutidines are predicted by theory, six dimethyl- and three ethyl-pyridines. Only two of the former are known. On the other hand, six pyridine-dicarbonic acids have been isolated. We can conceive of the formation of collidines by replacing the hydrogen of pyridine either by three methyl groups, by one propyl group, one isopropyl group, or by one methyl and one ethyl group. There are thus possible six trimethyl pyridines, three propyl pyridines, three isopropyl pyridines and ten methyl ethyl pyridines; in all, twenty-two collidines. A number of these are already known, but our knowledge of their properties, physical constants, and especially their oxidation products, is so limited that at present it is impossible to classify them.

The homologues of pyridine and of quinoline, as well as quinoline itself and certain natural alkaloids, such as quinine, cinchonine, nicotine, etc., when oxidized yield nitrogenous acids, which may be regarded as carboxyl derivatives of pyridine. Distilled with lime they give pyridine just as benzoic, phthalic acids, etc., under the same conditions give benzene. Pyridine itself offers a much greater resistance to oxidizing agents than benzene; chromic acid, and even boiling fuming nitric acid have no effect upon it. Huber first obtained nicotinic acid (pyridine monocarbonic acid) by oxi-

[1] Annalen der Chemie, **155**, 297.
[2] Berichte der deutschen chemischen Gesellschaft, **3**, 202.
[3] Comptes Rendus, **88**, 454.
[4] Monatshefte für Chemie, **1**, 41.

dizing nicotine, and in 1871 Dewar obtained the same acid by the oxidation of α picoline. By oxidizing the mixture of picolines contained in bone oil Weidel[1] obtained two isomeric pyridine monocarbonic acids, which he calls nicotinic and picolic acids, and by oxidizing lutidine Weidel and Herzig[2] succeeded in isolating the third isomer possible, which they call isonicotinic acid. Wischnegradsky[3] oxidized the aldehyde collidine of Baeyer, and obtained a methyl-pyridine-dicarbonic acid; while Hoogewerf and van Dorp[4] have obtained pyridine tricarbonic acid by oxidizing quinine and cinchonine with potassium permanganate. A second acid of this composition has been obtained by Böttinger[5] from uvitonic acid.

The pyridine bases have the power of uniting directly with two, four or six atoms of hydrogen. Wischnegradsky[6] has described a hexahydrolutidine which has the properties of a secondary base. The isochlor-pyridine of Ciamician and Dennstedt[7] can also unite with six atoms of hydrogen. Hofmann[8] has devised a general method for building up the hydropyridines. By distilling a mixture of a pyridine ammonium iodide with potassium hydroxide, oxygen is liberated, potassium iodide formed, and the hydrogen of the hydroxide takes the place of the iodine in the base. Thus with the iodide of methyl-pyridylammonium this reaction takes place,

$$\underset{\text{Methyl pyridyl ammonium iodide.}}{C_5H_5N.CH_3I} + KOH = O + KI + \underset{\text{Dihydro-picoline.}}{C_5H_5NCH_3H}$$

As these hydro-bases can be readily transformed into the bases themselves, the reaction of Hofmann becomes the more valuable, because it enables us to pass directly from any member of the series to the next higher.

According to Wischnegradsky the pyridine bases exist in the state of hydrides in the alkaloids. From the labors of Königs[9] and of Schotten[10] we know that piperidine is hexahydropyridine, and more recently Oeschner de Koninck[11] has found tetrahydroquinoline in the crude quinoline obtained by distilling cinchonine with sodium hydroxide. The researches of Cahours and Etard have shown that nicotine is a tetrahydroisodipyridine, while further evidence in favor of this idea is to be found in the work of Weidel and Russo.[12] Starting with pyridine C_5H_5N, treating with metallic sodium, they obtained dipyridyl $C_{10}H_8N_2$. Treated with nascent hydrogen dipyridyl takes up six atoms, and there is formed isonicotine, $C_{10}H_{14}N_2$.

[1] Berichte der deutschen chemischen Gesellschaft, **12**, 1989.
[2] Monatshefte für Chemie, **1**, 48.
[3] Berichte der deutschen chemischen Gesellschaft, **12**, 1506.
[4] Annalen der Chemie, **204**, 84.
[5] Berichte der deutschen chemischen Gesellschaft, **13**, 2048, and **14**, 134.
[6] Bulletin de la Société Chimique, **34**, 340.
[7] Berichte der deutschen chemischen Gesellschaft, **14**, 1153. [8] *Ibid.* **14**, 1497. [9] *Ibid.* **12**, 2341.
[10] *Ibid.* **15**, 421. [11] Annales de Chimie et de Physique (5), **27**, 433.
[12] Monatshefte für Chemie, **3**, 850.

A number of substitution products of pyridine are known. Hofmann, Anderson and Ciamician and Dennstedt have described chlorine and bromine derivatives. O. Fischer[1] obtained pyridine-sulphonic acid by heating pyridine with an excess of concentrated sulphuric acid, and from this, by means of well-known reactions, he prepared the cyanide and the corresponding acid.

Quinoline Series, $C_nH_{2n-11}N$.—By distilling quinine, cinchonine or strychnine with potassium hydroxide, Gerhardt[2] obtained a substance having the properties of an energetic base which he called quinoline. Two years previous, in 1843, Runge had discovered leucoline, a base of the same composition occurring in coal tar. Hofmann[3] finding that leucoline and quinoline gave the same crystalline precipitate with chromic acid, concluded that the two bases were identical. The study of these compounds was undertaken in 1860 by C. G. Williams, and he succeeded in isolating the parallel series of homologous bases as follows:

Quinoline,	C_9H_7N	Leucoline.
Lepidine,	$C_{10}H_9N$	Iridoline.
Dispoline,	$C_{11}H_{11}N$	Cryptidine.
Tetrahiroline,	$C_{12}H_{13}N$	

By the decomposition of the alkaloids with caustic potassa, bases of the first series are exclusively formed, while the members of the second series occur in coal tar. In properties these bodies resemble the pyridine bases. Towards alkyl iodides they act like tertiary amines, and on oxidation they are transformed into pyridine carbonic acids. Pure quinoline, free from its homologues, may be prepared by heating cinchonine with copper oxide and caustic potassa.[4] Königs[5] has made it synthetically by passing the vapor of allyl-aniline, $C_6H_5NHC_3H_5$, over heated lead oxide. Baeyer[6] by treating hydrocarbostyril with phosphorus pentachloride, obtained dichlorquinoline, which by nascent hydrogen was converted into quinoline. The dry distillation of acridate of calcium, or of acrolein-aniline, also yields quinoline.[7] Böttinger[8] states that the hydrochlorate of aniluvitonic acid when heated with soda lime is converted into quinoline. But these methods are only of scientific interest, and it is to the work of Skraup[9] that we owe a process for the synthesis of quinoline and its homologues which is not only of the greatest theoretical value and of general application, but at the same time it is an economical method for the production of these bases in quantity. The details of the process have been described in a previous volume of this Journal.[10]

[1] Berichte der deutschen chemischen Gesellschaft, **15**, 62.
[2] Annalen der Chemie, **42**, 310, and **44**, 279. [3] *Ibid.* **53**, 427.
[4] Wischnegradsky, Berichte der deutschen chemischen Gesellschaft, **13**, 2318.
[5] *Ibid.* **12**, 453. [6] *Ibid.* **12**, 1320. [7] Graebe and Caro, *Ibid.* **13**, 99. [8] *Ibid.* **13**, 2165.
[9] Monatshefte für Chemie, **1**, 316, and **2**, 139 and 171. [10] See this Journal, **4**, 63.

The synthesis of lepidine, the second member of the series, has been effected by Döbner and Miller.[1] The method is analogous to that of Skraup, and consists in heating a mixture of aniline, nitrobenzene, sulphuric acid and glycol or paraldehyde.

The quinoline bases when oxidized are transformed into pyridine-carbonic acids, quinoline itself yielding cinchomeronic acid or pyridine-dicarbonic acid. This fact indicates a close connection between the quinoline bases and such alkaloids as quinine, cinchonine and their isomers, because these two when oxidized are converted into pyridine di or tricarbonic acids. Quinoline, like the pyridine bases, has the power of forming hydrides by treatment with tin and hydrochloric acid. Wischnegradsky[2] obtained from it tetrahydroquinoline, and Jackson[3] has also described a tetrahydroquinoline, both of which are secondary bases. They are very unstable substances, and the weakest oxidizing agents change them back into quinoline.

Among the substitution-products of quinoline are the oxyquinolines or quinophenols analogous to the naphthols in their mode of formation, properties and general reactions. Nitroquinoline, like nitronaphthalene, readily yields the amine, and the cyanogen derivatives can be transformed in the usual way into the quinoline-carbonic acids. In fact, the synthesis of quinoline and the analogies existing between its derivatives and those of naphthalene seem to justify Körner's structural formula. According to his hypothesis quinoline has a structure analogous to that of naphthalene, and bearing the same relation to pyridine that naphthalene does to benzene; and as one of the CH groups of naphthalene is supposed to be replaced by an atom of nitrogen, we see the possibility of two such substances corresponding with the α and β monosubstitution products of naphthalene. Because of its formation from dichlorquinoline Baeyer regards quinoline and its homologues as belonging to the α series; leucoline and its homologues would hence belong to the β series. But it is still an open question whether leucoline is really isomeric with quinoline. Hofmann regarded them as identical, but C. G. Williams pointed out that quinoline with amyl iodide yields the blue coloring matter cyanine, while leucoline has not this property. Hoogewerf and Van Dorp[4] have confirmed the statement of Williams; but, on the other hand, quinoline and leucoline when oxidized with potassium permanganate give the same pyridine-dicarbonic acid.

E. H. K.

[1] Berichte der deutschen chemischen Gesellschaft, **14**, 2812.
[2] Bulletin de la Société Chimique, **34**, 340.
[3] Berichte der deutschen chemischen Gesellschaft, **14**, 889.
[4] Annalen der Chemie, **204**, 117.

Researches on Caffeine.

Although, since the celebrated work of Liebig and Wöhler, uric acid has been a frequent subject of investigation, a comparatively small amount of study has been devoted to the allied bases, caffeine, theobromine, xanthine and guanine. In the hope now of throwing light on the nature of uric acid Emil Fischer[1] has undertaken a careful study of caffeine and has reached results of considerable interest and importance. An abstract of Fischer's paper is here given.

That some connection exists between uric acid and caffeine was shown by the early investigations of Stenhouse[2] and of Rochleder.[3] By oxidizing caffeine with nitric acid the former obtained nitrotheine or cholestrophane, which was afterward recognized as dimethyl-parabanic acid. He also observed in the same reaction the formation of a substance which yielded a purple color with ammonia, similar to that of murexide. Rochleder investigated the conduct of caffeine towards moist chlorine, and discovered chlorcaffeine and amalic acid. He was struck by the similarity of this substance to alloxantin, and Strecker showed it to be a methyl derivative of alloxantin. This observation of Rochleder forms the basis of Fischer's investigation.

The principal new facts established are the following:

1. By careful oxidation with chlorine, caffeine yields dimethyl-alloxan and methyl-urea:

$$\underset{\text{Caffeine.}}{C_8H_{10}N_4O_2} + 2O + 2H_2O = \underset{\text{Dimethyl-alloxan.}}{C_6H_8N_2O_5} + \underset{\text{Methyl-urea.}}{C_2H_6N_2O}.$$

2. By reduction with hydrogen sulphide, dimethyl-alloxan yields amalic acid (tetramethyl-alloxantin); and this by careful oxidation with nitric acid again yields dimethyl-alloxan.

3. There is one atom of hydrogen in caffeine which differs from the others in being easily replaced by the ordinary substituting groups. Among the products described is hydroxy-caffeine, $C_8H_9(HO)N_4O_2$.

4. Caffeine easily takes up two atoms of bromine, forming an addition-product. Hydroxy-caffeine acts in the same way. If the latter action takes place in the presence of alcohol, a diethoxy-derivative is formed, thus:

$$C_8H_9(HO)N_4O_2 + 2C_2H_4O + 2Br = 2HBr + C_8H_9(HO).N_4O_2(OC_2H_5)_2.$$

5. Diethoxy-hydroxy-caffeine, when treated with warm hydrochloric acid, is converted into two new bodies, apo-caffeine, $C_7H_7N_3O_5$, and hypo-caffeine, $C_6H_7N_3O_2$.

6. Apo-caffeine, $C_7H_7N_3O_5$, when boiled with water, yields carbon dioxide and caffuric acid:

$$\underset{\text{Apo-caffeine.}}{C_7H_7N_3O_6} + H_2O = CO_2 + \underset{\text{Caffuric acid.}}{C_6H_9N_3O_4}$$

[1] Annalen der Chemie, **215**, 253. [2] *Ibid.* **45**, 366; and **46**, 272. [3] *Ibid.* **69**, 190; and **71**, 1.

7. Caffuric acid is decomposed when heated with basic acetate of lead, yielding mesoxalic acid, methylamine and methyl-urea:

$$\underset{\text{Caffuric acid.}}{C_6H_9N_3O_4} + 3H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_4O_6} + \underset{\text{Methyl-amine.}}{CH_3NH_2} + \underset{\text{Methyl-urea.}}{C_2H_6N_2O}$$

8. When treated with fuming hydriodic acid, caffuric acid is converted into hydro-caffuric acid, $C_6H_9N_3O_3$, which breaks up into methylamine and an acid which in turn readily yields methyl-hydantoïne, $C_4H_6N_2O_2$, and carbon dioxide. This series of transformations indicates that in caffeïne there is not only the alloxan nucleus, but also the carbon-nitrogen nucleus of methyl-hydantoïne.

9. Hypo-caffeïne, $C_6H_7N_3O_3$ (see 5), is broken up, when heated with water at 150°, or when treated with bases at a lower temperature, yielding carbon dioxide and caffoline, $C_5H_9N_3O_2$; and this, treated with hydriodic acid, yields methyl-urea and another product.

10. Caffoline, $C_5H_9N_3O_2$, is converted into methyl-oxamic acid and methyl-urea when oxidized with an alkaline solution of potassium ferricyanide:

$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O + H_2O = \underset{\text{Methyl-oxamic acid.}}{CH_3.NH.CO.CO_2H} + \underset{\text{Methyl-urea.}}{CH_3.NH.CONH_2}$$

With an alkaline solution of potassium permanganate it yields dimethyl-oxamide:

$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O + H_2O = \begin{matrix} CO.NH.CH_3 \\ | \\ CO.NH.CH_3 \\ \text{Dimethyl-oxamide.} \end{matrix} + CO_2 + NH_3$$

Chromic acid converts it into cholestrophane:

$$\underset{\text{Caffoline.}}{C_5H_9N_3O_2} + O = \underset{\text{Cholestrophane.}}{C_5H_6N_2O_2} + NH_3.$$

These transformations lead to the conclusion that in caffoline the group, $\begin{matrix} C-N\,CH_3 \\ | \quad\quad > CO \\ C-N \end{matrix}$, is present, and that its formula is

$$\begin{matrix} HO.HC-N\,CH_3 \\ | \quad\quad > CO \\ CH_3.HN-C=N \end{matrix}$$

Taking all the above facts and conclusions into consideration, Fischer suggests as the formula of caffeïne,

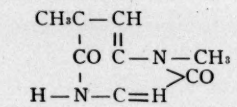
$$\begin{matrix} CH_3-N-CH \\ | \quad\quad || \\ CO \quad C-N\,CH_3 \\ | \quad\quad | \quad\quad > CO \\ CH_3-N-C=N \end{matrix}$$

A careful examination of this formula will show that it is what it ought to be, and nothing more, an expression in chemical language of facts previously established.

Theobromine, the lower homologue of caffeïne, may be transformed into the latter by the introduction of a methyl group. But as caffeïne contains three methyl groups united to nitrogen, the question remains open, which one is lacking in theobromine. By oxidation with chromic acid, dimethyl-parabanic acid is obtained from caffeïne, and mono-methyl-parabanic acid from theobromine.

When treated with chlorine, caffeïne breaks up into monomethyl-urea and dimethyl-alloxan, while theobromine yields monomethyl-alloxan.

Only one methyl group in theobromine is, therefore, in the alloxan nucleus; and since it is split off in forming apo- and hypo compounds, it is the one indicated by (*a*) in the formula for caffeïne. The formula for theobromine is therefore



The similarity of xanthine to theobromine was noticed by Strecker some time ago, but he was unable to transform it into one or the other by adding methyl. But Fischer has effected the synthesis of theobromine by treating the lead compound of xanthine with methyl iodide. He has also shown that the action of chlorine on xanthine is analogous to the action of chlorine on caffeïne and theobromine, urea and alloxan being formed. This fact furnishes the desired experimental demonstration that theobromine is the dimethyl, and caffeïne the trimethyl, derivative of xanthine. D. T. D.

NOTES.

On the Oxidation of Cork Stoppers and Rubber Joints.[1]

Dear Sir: The remarks of Keiser and yourself[2] on a source of error in experimentation due to the formation of carbon dioxide by the action of ozone on cork stoppers and rubber connecters, of the apparatus employed, suggest to me that I have too long neglected to bear witness to the accuracy of the observation of H. Karsten, to the effect that such connecters are constantly liable

[1] A letter to the Editor.

[2] Remsen and Keiser, this Journal, **4**, 456.

to oxidation even in mere air and at the ordinary temperature. In a paper "On the extreme difficulty of removing the last traces of carbonic acid from large quantities of air," published in 1860 by C. W. Eliot[1] and myself, we remarked incidentally that Karsten had apparently not allowed for this particular difficulty in some experiments published by him[2] in that year "On the action of oxygen on non-nitrogenous organic substances," to which criticism Karsten made reply[3] by suggesting that we were ourselves at fault in not having allowed for the contact of air with the organic matter of the corks and connecters of our apparatus. He described experiments, withal, by which the presence of carbonic acid was exhibited in air that had been passed through rubber tubing, and verified his earlier work by performing similar experiments in apparatus specially designed to avoid this source of error. At the first opportunity that presented itself to me, which was not until 1870, I repeated Karsten's experiment and satisfied myself of the entire accuracy of it. For example, on pushing, slowly, 179,500 cc. of air through the apparatus described by Karsten, absolutely no precipitate of carbonate of lime was obtained in the lime water, nor was any precipitate formed when 150,000 cc. of air were drawn through the apparatus by means of an aspirator. The apparatus in question is arranged in such manner that all the connecters are shielded from contact with the air. Moreover, the air was passed through ignited oxide of copper, to destroy oxidizable carbonaceous matters before it came to the potash bulbs proper to remove carbonic acid at the anterior part of the apparatus. *Per contra*, I did obtain precipitates of calcic carbonate in the lime water on aspirating the purified air through the apparatus arranged as just now described, with the exception that its joints were not specially protected from contact with air. Under these conditions 150,000 cc. of the air gave a slight precipitate, and 180,000 cc. gave a considerable precipitate.

It follows, of course, that if cork stoppers can be slowly oxidized by mere air, they must in certain cases be carefully protected from ozone, as the experiments of Keiser and yourself have so clearly shown. Karsten[4] found a fourfold increase in the yield of carbonic acid when his non-nitrogenous substances were exposed to air ozonized by phosphorus, instead of to ordinary atmospheric air.

F. H. STORER.

BUSSEY INSTITUTION, JAMAICA PLAIN, MASS., *April* 2, 1883.

Carbonic Acid.

M. BALLO has endeavored to answer the question whether the hypothetical carbonic acid is present in solutions of carbon dioxide in water, by introducing into such solutions pieces of magnesium

[1] Proceedings of the American Academy, **5**, 62.
[2] Poggendorf's Annalen, **109**, 346.
[3] *Ibid.* **115**, 348.
[4] *Ibid.* **109**, 351.

ribbon. He first showed that magnesium does not act upon water itself, even at the boiling temperature. On then introducing the metal into carbonic acid, a slow evolution of hydrogen soon began at the ordinary temperature and continued regularly for some time. The facts that at ordinary temperatures a large amount of carbon dioxide remains in solution in water and that there is a gradual decomposition, are in accordance with the assumption that there is actually a compound present. Acid carbonates in solutions also dissolve magnesium.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 3003.)

The Atomic Refraction of Sulphur.

R. NASINI has studied a number of sulphur compounds with reference to their refractive power, and has found that sulphur has at least two refractive equivalents. Brühl[1] has shown that carbon, in the usual condition of combination, has one refractive equivalent, and in the condition called "double linkage" another; and that oxygen also has two values according to whether it is present in a compound in the hydroxyl condition or the carboxyl condition. The results obtained by Nasini for sulphur are similar to those obtained by Brühl for carbon and for oxygen. The number of sulphur compounds studied is limited, so that the values given do not depend upon as many accurate measurements as do those for carbon and oxygen. In such compounds as ethyl mercaptan, $C_2H_5(SH)$, ethyl sulphide, $(C_2H_5)_2S$, etc., the refractive equivalent is 7.65; while in such as CS_2 and $CS(OC_2H_5)_2$ it is 8.84.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2878.)

Relations between Boiling Points and Specific Volumes.

W. STAEDEL has made an elaborate study of the chlorine substitution products of ethane, and has succeeded in showing that simple relations exist between the figures representing the boiling points and those representing the specific volumes. To illustrate the character of the relations a few examples may be cited. The boiling point of the substance $\begin{matrix}CH_3\\|\\CHCl_2\end{matrix}$, under a pressure of 400 mm., is 39.607°; that of $\begin{matrix}CH_2Cl\\|\\CHCl_2\end{matrix}$ is 92.758°. The difference is a fraction more than 53°. That is, an elevation in the boiling point of about 53° is effected by the substitution of the first hydrogen atom in the group CH_3. A number of similar cases show that this is a general rule, so far at least as the compounds examined are concerned. Secondly, the compound, $\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$, boils at 64.733° (400

[1] See this Journal, **3**, 352.

mm. barom.), while the compound, $\begin{matrix}CH_2Cl\\|\\CHCl_2\end{matrix}$, boils at 92.758°. Here the difference is about 28°. Thus it will be seen that the introduction of the second chlorine atom into CH_2Cl causes an elevation in the boiling point of 28°. Finally, $\begin{matrix}CH_2Cl\\|\\CHCl_2\end{matrix}$ boils at 92.758° and $\begin{matrix}CH_2Cl\\|\\CCl_3\end{matrix}$ at 108.127°. The difference is something more than 15°; or by the introduction of the third chlorine atom the boiling point is raised about 15°. All the possible illustrations of these regularities furnished by the chlorine products of ethane are studied and the rules above given found to be true in all cases except one. Similar regularities were observed in connection with the specific volumes. The exact values found corresponding to the normal pressure (760 mm.) are here given. For the boiling points,

$$B(cl_1 - h) = 56.22$$
$$B(cl_2 - h) = 31.30$$
$$B(cl_3 - h) = 16.04$$

For the specific volumes,

$$S(cl_1 - h) = 14.20$$
$$S(cl_2 - h) = 16.37$$
$$S(cl_3 - h) = 19.16$$

These equations express the changes in the boiling points (B) and the specific volumes (S) effected by introducing into a substance one chlorine for the first hydrogen ($cl_1 - h$); a chlorine atom for the second hydrogen ($cl_2 - h$); and a chlorine atom for a third hydrogen ($cl_3 - h$).

It appears from these results that a chlorine atom may have different "boiling values" and different specific volumes. Either this is true, or carbon, or hydrogen or both have different values in isomeric compounds. Hence the assumption of the constancy of the specific volumes even of the univalent elements appears somewhat unjustifiable.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2559.)

Estimation of Vapor Densities.

VICTOR MEYER cautions chemists against too general a use of his simple method for the estimation of specific gravities of vapors, and calls attention to the title of his first paper describing the method. The title is, "On the estimation of vapor densities of bodies boiling above 440°, as well as of bodies which attack mercury or Wood's metal." Meyer says that the use of the method should be restricted to cases in which the exact methods of Gay Lussac, Dumas and Hofmann cannot be used.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2778.)

Note on the Test for Tin mentioned in this Journal, 4, 474.

I find that iron wire works much more satisfactorily than copper. Ferrous chloride does not reduce mercuric chloride. Stannic chloride alone, or in the presence of antimony, or of antimony and arsenic, is reduced to stannous chloride and gives the test with mercuric chloride. Arsenic in the absence of antimony prevents the reduction, but if enough antimony is present so that metallic antimony is precipitated, the stannic chloride will be reduced at the same time. The presence of much arsenic will entirely prevent the precipitation of a little antimony, but tin can be detected after the addition of enough antimony chloride so that metallic antimony is precipitated on boiling with iron. This test is essentially the same as a process given by Fresenius for the quantitative separation of antimony and tin. It is found to work well as a qualitative test in the hands of students, which cannot be said of the usual process, based on the reduction to metallic tin by means of zinc and platinum. W. A. NOYES.

Fermentation of Cellulose.

F. HOPPE SEYLER has proved conclusively that in sewage there is a ferment which has the power of converting cellulose into marsh gas and carbon dioxide. A small quantity of sewage, the amount of organic matter in which had been previously determined, was brought into a flask with a known quantity of cellulose and distilled water. The gases given off were carefully measured and analyzed, and it was thus found that the cellulose was certainly transformed into marsh gas and carbon dioxide. The evolution of gases continued thirteen months, and was still in progress. As the ferment involved in this action is found in all kinds of refuse organic matter, this fermentation of cellulose must be going on to an enormous extent on the surface of the earth.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 122.)

Quinoline derivatives in Medicine.

OTTO FISCHER has recently patented processes for making certain derivatives of quinoline. Oxyquinoline and methoxyquinoline prepared from quinolinesulphonic acid can be converted by reducing agents into tetrahydro-compounds. The tetrahydrides are converted into methyl and ethyl derivatives when treated with the corresponding iodides, and these derivatives are tertiary bases:

$$\underset{\text{Oxyquinoline tetrahydride.}}{C_9H_{11}NO} + CH_3I = HI + C_{10}H_{13}NO$$

β-Oxyhydromethylquinoline crystallizes and forms easily soluble salts. This compound as well as some others similar to it have strong anti-febrile properties, and may be used as satisfactory substitutes for quinine.